

1

2,970,906

XEROGRAPHIC PLATE AND A PROCESS OF COPY-MAKING

William E. Bixby, Columbus, Ohio, assignor, by mesne assignments, to Haloid Xerox Inc., Rochester, N.Y., a corporation of New York

No Drawing. Filed Aug. 5, 1955, Ser. No. 526,781

19 Claims. (Cl. 96—1)

This invention relates in general to an electrophotographic member, and in particular to a member for electrophotography, having a conductive backing and a thin photoconductive insulating coating of uniform characteristics whereby an electrostatic latent image of faithful reproductive quality can be formed on the surface thereof. Such images may, for example, be developed on the plate, transferred to paper and fixed there, when copy-making is the object, or developed and retained on the plate itself, when rapid X-ray images are desired, or otherwise.

This application is a continuation-in-part of my co-pending application Ser. No. 206,129, filed January 15, 1951, which was a continuation-in-part of my earlier applications Ser. No. 37,532, filed July 1, 1948, and Ser. No. 46,678, filed August 28, 1948, which were co-pending with Ser. No. 206,129, each of the aforementioned applications being now abandoned.

In Carlson U.S. Patent 2,297,691 there was disclosed a new electrophotographic process which has since been developed toward commercial applications under the name xerography. According to this process, a plate comprising a photoconductive insulating coating on a conductive backing is provided with an electrostatic charge and is then exposed to a light image, whereupon the coating becomes conductive under the influence of light and the electrostatic charge is selectively dissipated to leave an electrostatic latent image corresponding to the dark portions of the optical image. Since the invention of this process, and with its development toward commercial use, there has been an increasing demand for xerographic or electrophotographic members or plates of increased sensitivity and uniformity, to be adaptable to the improved xerographic process. In particular it has become desirable to have electrophotographic plates suitable for continuous-tone photography and suitable for copying of line images such as drawings, manuscripts, letters, documents, and the like.

Now, in accordance with the present invention, there is provided a substantially improved new electrophotographic member such as a plate of dimensions, uniformity and sensitivity operable for photographing, copying and printing and adapted for use with an electrophotographic process, the member comprising a metallic or conductive support member having a coating thereon of a thin layer of vitreous selenium in uniform state and of uniform characteristics within its effective boundaries, whereby a uniform electrostatic charge or potential may be imparted to the coating over the entire area of the image surface and whereby a uniform and predetermined rate of conductivity is imparted to the photoconductive layer by exposure to measured illumination. Specifically, an electrophotographic member is prepared on a smooth conductive backing material, such as for example a clean mirror-finished metallic plate on which the photoconductive coating consists of a layer continuous throughout the entire area within its effective boundaries and uniform within such area, the coating being vitreous sele-

2

nium, with a thickness between about 10 and about 75 microns for copymaking by tungsten light and up to 160 microns or more for X-ray use, and uniform over its area within a tolerance of about 20 percent. The surface of the member is characterized by having a mirror-like finish and by being free from visible, macroscopic imperfections, and preferably having a metallic or conductive border surrounding the selenium layer to make the product more suited to commercial applications. The photoconductive insulating coating is capable of receiving a substantially uniform electrostatic charge by exposure to a constant voltage corona spray, generally being able to receive and retain over its entire area a charge of about 300 volts and usually at least about 400 volts, and to retain throughout the entire effective area, for at least one minute in the absence of illumination, about 80 percent of the original charge in the case of plates for manual use, and about half or more of the original charge in the case of plates for use in automatic copying machines. Otherwise stated, the rate of charge dissipation in darkness is usually less than 20% per minute, or .33% per second, but this may not be true in the case of plates fatigued by long use or by intense illumination whose charge dissipation rate in darkness may rise to a much higher figure till the plate is no longer useful. The conductivity of the photoconductive insulating coating when exposed to light is such as to result in a charge dissipation rate of from about 4 percent to about 12 percent or more, depending on the thickness of the selenium coating, on exposure to one meter candle second of light from a tungsten filament source (at about 2400° K.) over the range between substantially the maximum charge acceptance at the upper end of the voltage range and 100 volts or lower at the lower end of the range.

According to one method of producing an electrophotographic member within the scope of this invention, substantially pure selenium is evaporated onto a metallic plate under conditions of high vacuum, for example, in a bell jar. In one specific embodiment of this method, the coating may be accomplished by conducting vaporized selenium from a body of selenium to a plate in an upwardly directed path for approximately 10 minutes while maintaining the plate at a temperature of about 100° C. and up to 120° C. as disclosed in my co-pending application Ser. No. 46,678, filed August 28, 1948. It will be understood, of course, that selenium-coated plates within the scope of this invention may be prepared by other methods for the deposition of vitreous selenium onto a conductive surface, such as spraying or hot pressing selenium thereon, the criteria being the ability of the methods to yield uniform vitreous selenium coatings of the necessary electrical characteristics.

The exact molecular structure of the selenium coating on the plate according to this invention is not known with certainty. The selenium coating or layer on the plate is present in a form or mixture of forms which presents a vitreous or glassy appearance and, in general, is characterized by a dark red appearance approaching a black color as seen by the human eye in ordinary illumination. It is believed that the selenium is present substantially in an amorphous form containing minor proportions of a crystalline form of selenium, although it is not desired to restrict this invention to the presence of such a mixture of forms. The appearance and therefore the molecular structure of the selenium is to be distinguished from the commonly known metallic or crystalline forms in which the element has a shiny metallic luster or a satiny gray finish. The selenium should be substantially free of impurities such as halides which, in amounts more than a few parts per million, promote the conversion of the selenium into the crystalline

metallic form with consequent loss of properties useful in this invention.

The electrophotographic member according to this invention may be in any desired physical form such as a plate, a cylinder, a flexible sheet, or other structure. However, for simplicity, the invention will be described in relation to a plate or other plane surface, with the realization that other structure may be substituted therefor without departing from the scope and spirit of the invention. In this manner, suitable backing members include metals and metallic plates such as aluminum, magnesium, brass, steel, and the like, and conductively-coated members such as conductively-coated glass, paper, plastic sheeting and the like. In addition, certain low-conductivity materials generally not considered as conductors may form the backing member, provided that their electrical resistance is at least several orders of magnitude lower than the resistance of the illuminated vitreous selenium, materials of this sort including glass, paper, and the like without conductive coating specially applied thereon.

For manual operation in a xerographic process it is necessary that the electrophotographic plate have certain physical and electrical characteristics which are essential for optimum results. For example, the xerographic plate which is used in the process may operate not only as an image receiving surface, but also as a printing surface, whereby an electrostatic latent image is received on the plate and is developed thereon to yield a physical image which in turn is transferred or printed onto a receiving surface. It is apparent, therefore, that for continuous-tone photography the plate must be of a size sufficient not only to receive the image but to print the image in dimensions suitable for photography. For this purpose, a minimum dimension for the usable vitreous selenium surface is at least about 3". According to the application of xerography to photocopying, the electrophotographic plate must be of a size to receive an image corresponding to letters, documents and the like, and to print such an image in its original size. It is, therefore, a commercially essential requirement for this purpose that the electrophotographic plate must have a usable minimum dimension of at least the width of material to be copied or, in other words, a usable minimum dimension of at least about 8 inches.

As the next requirement of an electrophotographic plate, it is observed that a high degree of uniformity is required, this uniformity requirement not decreasing as the size of the plate is increased. Thus, an electrophotographic plate of dimensions suitable for the process must be highly uniform and must be capable of accepting a uniform charge over its entire surface. If the charge acceptance is low in one area and high at another area on the plate, it is readily apparent that the highly chargeable area will receive a greater electrostatic charge than other areas and will therefore attract larger amounts of the developer material, resulting in a dark area on the print. In a similar manner, if the charge dissipation or conductivity of the plate varies in different areas thereon, uneven density of the print will be noted or emphasized. In particular, manually-operated xerographic processes may be carried out over an operation period of 5 to 10 minutes, and occasionally up to one or several hours, during which a plate will be charged or provided with an electrostatic charge which may be in the general range of about 75 to about 500 volts. The charged plate is then exposed and developed, during which time dissipation of the charge can occur even in the absence of illumination. The result of this is that the voltages on the various areas of the plate can vary more widely as a result of the charge acceptance and dark decay (rate of dissipation of electrical charge in the absence of illumination) than they do because of the applied voltage during charging or because

of variations in the illumination during exposure. It is therefore essential that the plate be electrically uniform over its entire area within a tolerance of about 20 percent and preferably within plus or minus 5 percent. One major contributing cause to nonuniformity of electrical characteristics is, of course, physical thickness of the selenium coating, and for this reason the coating itself must be substantially uniform, generally within a tolerance of plus or minus 20 percent.

Another commercially important characteristic of the electrophotographic plate is its sensitivity, which may be expressed in terms of rate of dissipation of applied charge during exposure to a measured illumination. Since the rate of dissipation of charge appears to be substantially directly proportional to the applied voltage within limits of operating conditions, this rate of dissipation may be expressed in terms of volts dissipated per volt of applied charge or as percent dissipation during a standard degree of illumination suitably expressed in meter candle seconds. Thus, a sensitivity expressed in terms such as .1 volt dissipated per volt of original charge by an exposure of one meter candle second, in practical terms signifies that a light exposure of one meter candle second results in 10 percent charge dissipation. It has been found that a sensitivity of about 10 percent per meter candle second will permit contact copying of letters, documents and the like by a short exposure to a convenient-sized tungsten light source; for camera photography such sensitivity is generally comparable with a relatively slow photographic film.

As an illustration of sensitivity of electrophotographic plates according to this invention, a series of such plates was prepared by exposing a clean, mirror-finished aluminum plate to selenium vapor under a high vacuum to produce a vitreous selenium coating on the plates having a thickness averaging about 20 microns and being at all points between about 16 and about 24 microns. The plates thus prepared would accept a charge greater than 300 volts, and in fact accepting a charge of at least 450 volts at all areas when exposed to a corona spray, thus being adapted to normal operating conditions and affording reasonable latitude of charge acceptance above and beyond the process requirements. These plates were exposed to a positive corona spray and charged to an average plate potential of about 550 volts as determined by means of an electrometer. The charged plates were then exposed to a light source consisting of a tungsten filament at about 2400° K. at a measured light intensity at the plate surface of 0.62 meter candle, the meter candle being adopted as the standard unit since its relatively low light intensity is most nearly in line with the exposure requirements of the new xerographic plates. At the end of this exposure time the plate voltage was again measured with the electrometer and the rate of charge dissipation thus determined. This procedure was repeated with successive exposures of ten seconds each to the light source followed by measurements of potential until the average plate voltage was under 100 volts. A similar series of tests was performed with a measured intensity of 0.304 meter candle and with a measured light intensity of 0.177 meter candle. In all instances during these particular tests a minimum sensitivity was noted to be greater than 0.1 volt per volt dissipation per meter candle second exposure, otherwise expressed as at least 10 percent dissipation for unit exposure.

As further illustrations of the sensitivity of electrophotographic plates made according to this invention, a series of such plates were made having selenium coatings of varying thicknesses, up to and including 160 microns. These plates, as shown by the examples below, had a sensitivity ranging from about 4 percent to about 12.5 percent for unit exposure.

It has been found that electrophotographic plates made according to the invention are subject to a form of fatigue affecting their charge retention in total darkness. In

5

plates freshly made the rate of charge dissipation in total darkness is negligibly small, and latent images will persist for several hours after exposure. In freshly made plates where the selenium thickness is about 20 microns, the ratio of charge dissipation under standard illumination to charge dissipation in darkness is in excess of 25, usually from 100 to 300 or more. In freshly made plates where the selenium is 160 microns thick the ratio exceeds 1000. However, the rate of charge dissipation in total darkness is increased by previous exposure of the plate to light or other radiation, which creates a condition that may be likened to fatigue. A similar condition exists in plates which have been subjected to prolonged use, as for example in automatic photocopying machines where the plate takes the form of a revolving drum on which images are formed and destroyed in each revolution. In such cases the dark charge retention capability of the plate may be greatly reduced, and in cases of severe artificially-induced fatigue the ratio falls toward and may become less than unity. While this tends to make backgrounds dark and text undecipherable, and calls for quick development before the image is lost, printed matter can be reproduced even under extreme conditions of this kind.

The following examples illustrate the foregoing:

Example 1

A freshly-made copymaking plate having a vitreous selenium layer about 20 microns thick was found to have a dark decay rate of 6.4% in 600 seconds (average 0.0107% per second) and a light decay of 10% in 2.5 seconds (4% per second) under standard unit illumination. The ratio of light to dark decay was 374.

Example 2

A plate similar to that mentioned in Example 1 was exposed to bright light for several minutes and then immediately tested for dark decay rate. This was found to have increased to 10% in 240 seconds (average 0.0416% per second) owing to fatigue. The decay rate under standard illumination appeared to be unchanged, and the ratio of the two rates was 96.

Example 3

A fresh plate suitable for X-ray work having a vitreous selenium layer about 160 microns thick was found to have a dark decay rate of 7% in 600 seconds (average 0.0117% per second) and a light decay rate of 10% in 0.8 second (12.5% per second) under standard unit illumination. The ratio of light to dark decay was 1070.

Example 4

A plate similar to that mentioned in Example 3 was exposed to intense illumination for an extended period of time and immediately tested for light and dark decay rates. The dark decay rate was found to have increased to 20% in 8.4 seconds (average 2.38% per second) while the light decay rate remained 10% in 0.8 second (12.5% per second) as in Example 3. As a result of the heavy light fatigue, the ratio for this plate had fallen to about 5. It required rapid handling to avoid loss of image.

Example 5

A plate similar to that mentioned in Example 3 was exposed for 3 minutes to X-ray radiation at considerable intensity and immediately tested. The dark decay rate had increased to 20% loss in 2.7 seconds (average 7.4% per second) and the light decay rate had fallen to 10% loss in 1 second. In this case the ratio was about 1.35 and the plate, until time permitted it to recover somewhat from fatigue, would make decipherable copies of textual matter only with very rapid handling after charging.

In each of the foregoing examples standard unit illumination was illumination of one meter-candle-second of light from a tungsten filament source at about 2400° K., and the rate of "light decay" has been computed so as

6

to exclude the accompanying "dark decay" which occurs simultaneously therewith. The two decays are of course additive at any given point on the surface of the plate, and at least some photographic contrast is achieved whenever the sum of light and dark decay in an illuminated area is greater than dark decay in an adjacent non-illuminated area. Hence a ratio between them of less than unity may produce a decipherable print if the operation is handled quickly enough.

As can readily be seen, the light decay or sensitivity and the dark decay are independent factors, and at the same time their interrelationship expressed as the ratio of light decay to dark decay is a third commercially important factor. Thus, sensitivity taken alone must be high to permit speedy operation of the xerographic process. Also, dark decay taken alone must be low to permit normal delays in operation of the process without excessive loss of charge. Lastly, light decay should largely exceed dark decay so that photographic contrast can be achieved under normal working conditions. For this reason, independently of the individual light and dark decay rates, a sensitivity ratio in terms of rate of charge dissipation at one meter candle second (tungsten light source at about 2400° K.) as against charge dissipation in the dark should for best results be at least 25, and preferably at least 100.

It is realized, of course, that the electrical characteristics of the plate will be somewhat different with respect to positive charging or negative charging. The characteristics set forth and defined herein are given in terms of an electrophotographic plate which is charged by means of a positive corona discharge, although the xerographic plates of this invention are suited for the xerographic process with either positive or negative corona charging or for charging by other means such as frictional charging and the like.

What is claimed is:

1. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a support member having at least one smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive insulating vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within the image area, a charge acceptance in excess of about 300 volts, and a charge dissipation rate under one meter-candle-second of illumination at least about 25 times greater than its charge dissipation rate in darkness.

2. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a support member having at least one smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive insulating vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within the image area, a charge acceptance in excess of about 300 volts, a charge dissipation rate in darkness of less than about 20% per minute, and a charge dissipation rate under applied illumination exceeding said charge dissipation rate in darkness.

3. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a support member having at least one

smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive insulating vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within the image area, a charge acceptance in excess of about 300 volts, a charge dissipation rate in darkness of less than about 20% per minute, and a charge dissipation rate under one meter-candle-second of illumination at least 25 times greater than said charge dissipation rate in darkness.

4. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a support member having at least one smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive insulating vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within the image area, a charge acceptance in excess of about 300 volts, a charge dissipation rate in darkness of less than about 20% per minute and a charge dissipation rate under one meter-candle-second of illumination of more than about 4% per second.

5. A xerographic plate as described in claim 1 wherein the average thickness of the selenium layer is between about 10 and about 75 microns.

6. A xerographic plate as described in claim 1 wherein the support member comprises conductively coated glass.

7. A xerographic plate as described in claim 1 wherein the support member comprises aluminum.

8. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a support member having at least one smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive substantially halide-free vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within the image area, a charge dissipation rate in darkness less than about 20% per minute, and a charge dissipation rate under one meter-candle-second of illumination at least 25 times greater than said charge dissipation rate in darkness.

9. A xerographic plate capable of forming an electrostatic image developable with electroscopic marking material comprising a cylindrical support member having at least one smooth surface free from visible imperfections throughout the area within which said image is to be formed, at least said surface area having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium and, overlying and supported by said surface and in electrical contact therewith throughout said area, an adherent layer consisting essentially of reddish-black glassy-appearing photoconductive insulating vitreous selenium, said layer of selenium having a smooth exposed surface, a uniform thickness averaging more than about 10 microns within

the image area, a charge acceptance in excess of about 300 volts, and a charge dissipation rate under one meter-candle-second of illumination at least about 25 times greater than its charge dissipation rate in darkness.

10. A xerographic process comprising imposing an electrostatic field through a photoconductive insulating layer comprising predominantly vitreous selenium said photoconductive insulating layer being positioned in electrical contact with a non-light sensitive, electrically conductive backing and, while the field is imposed, selectively flowing charge through portions of the photoconductive insulating layer by selectively exposing said portions to activating radiation forming a varying charge pattern of intelligence to be reproduced which is adapted to be developed with marking material.

11. A process comprising the placing of electrostatic charges on a surface of a layer of vitreous selenium positioned in electrical contact with an electrically conductive backing and exposing said layer to activating radiation thereby rendering said vitreous selenium conductive in areas exposed and dissipating said electrostatic charges.

12. A process as in claim 11 wherein said activating radiation selectively dissipates said electrostatic charges.

13. A process of xerography in which electrostatic charges are distributed in image configuration on a surface of a layer of vitreous selenium positioned in electrical contact with an electrically conductive backing, said process comprising exposing said layer to activating radiation thereby rendering said vitreous selenium conductive in areas exposed dissipating electrostatic charges through the conductive vitreous selenium.

14. The method of xerography which comprises charging the surface of a layer of photoconductive insulating vitreous selenium with an electric charge, exposing the charged layer photographically while maintaining a conductive backing in contact with the surface of said layer opposite to said charged surface and then dusting the charged surface with an electrostatically attractable, finely-divided material to develop the charged image.

15. The method of making a photographic reproduction which comprises applying an electric field through a layer of photoconductive insulating vitreous selenium positioned in electrical contact with an electrically conductive backing and projecting an image onto said layer whereby a flow of electricity will take place through said layer producing an electrostatic latent image at a surface thereof and depositing dust particles on said surface where said particles will adhere in a distribution varying in density with the intensity of the charge at the various parts of the surface.

16. The process of copy-making which comprises uniformly charging, to a potential sufficient to attract electroscopic particles, the surface of an electrophotographic plate comprising a support member having an electrical resistance at least several orders of magnitude lower than the resistance of illuminated vitreous selenium, said member having a smooth surface and, overlying and supported by and in continuous electrical contact with said surface, a thin layer of substantially uniform thickness and mirror-smoothness consisting essentially of photoconductive insulating vitreous selenium having a rate of charge decay under one meter candle-second of illumination from a tungsten filament source at 2400° K. at least 25 times the rate in total darkness, and selectively dissipating said charge by exposing a surface of said selenium to a pattern of radiation to be copied.

17. The process described in claim 16 wherein the surface of the selenium is exposed to a pattern of visible light and shadow.

18. A process of producing an electrostatic image comprising placing an electrostatic charge on the photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having on at least one surface thereof a photoconductive insulating layer consisting essentially of vitreous selenium and

selectively dissipating electrostatic charge by exposing the charged surface of said xerographic member to an image pattern of light whereby there is created an electrostatic image corresponding to the light image.

19. In a xerographic process wherein an electrostatic charge is placed on the surface of a xerographic member comprising a photoconductive insulating layer overlying and in electrically conductive contact with a conductive backing member, selectively dissipating electric charge from the surface of the charged photoconductive insulating layer by exposing the charged layer to a light image thereby creating an electrostatic image on the surface of the photoconductive insulating layer and developing said electrostatic image by developer material attracted thereto by electrostatic charge on said surface, the improvement comprising using vitreous selenium as the photoconductive insulating layer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,199,104 Johnson et al. ----- Apr. 30, 1940

20

2,297,691
2,354,109
2,476,042
2,654,853
2,657,152
2,663,636

5

10

15

Carlson ----- Oct. 6, 1942
Flood ----- July 18, 1944
Hewlett ----- July 12, 1949
Weimer ----- Oct. 6, 1953
Mengali et al. ----- Oct. 27, 1953
Middleton ----- Dec. 22, 1953

OTHER REFERENCES

Nature, April 3, 1948, vol. 161, page 522.
Radio Craft for March 1943, page 334.
Nicholson: The Physical Review, vol. III, #1, 2nd series, pp. 1-23.
Foersterling: Chemical Abstracts, vol. 8, p. 3643 (1914).
Reimy: Treatise on Inorganic Chemistry, Elsevier, p. 742 (1957).
Schoop: Chemical Abstracts, vol. 4, p. 2235 (1910).
Wilcke: Photographische Korrespondenz, vol. 57, pp. 173-5.