Sept. 30, 1969 C. WOOD ET AL 3,469,978

PHOTOSENSITIVE ELEMENT

Filed Nov. 30, 1965

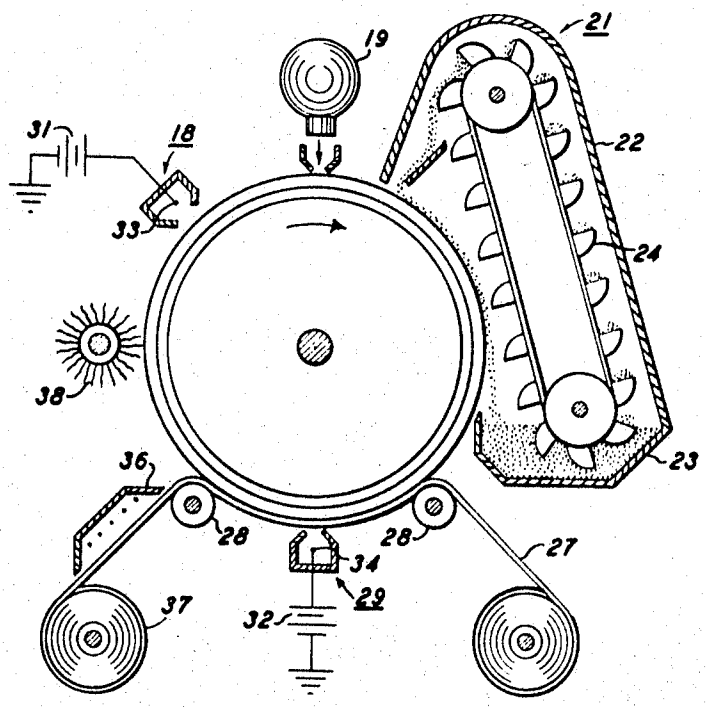


FIG. 1



FIG. 2

INVENTORS
CHARLES WOOD
G. SANJIV KAMATH
JAMES H. NEYHART
BY James J. Rabeneck
Stanley J. Cole
ATTORNEYS

United States Patent Office 3,469,978
Patented Sept. 30, 1969

3,469,978

PHOTOSENSITIVE ELEMENT

Charles Wood, Pittsford, G Sanjiv Kamath, Rochester, and James H. Neyhart, Penfield, N.Y., assignors to Xerox Corporation, Rochester, N.Y., a corporation of New York

Filed Nov. 30, 1965, Ser. No. 510,561
Int. Cl. G03g 7/00; C01b 25/00; C23c 13/00
U.S. Cl. 96—1.5 15 Claims

ABSTRACT OF THE DISCLOSURE

A xerographic plate comprising a supporting substrate having on one surface thereof a substantially binderless photoconductive insulating layer of at least one compound of the Group III–V elements, said substrate having an electrical resistance less than said photoconductive insulating layer, with said photoconductive insulating layer having a resistivity of at least about 10^{10} ohm-cm. and being capable of supporting an electrostatic charge in the dark and dissipating a portion of said charge in response to electromagnetic radiation impinging thereon.

This invention relates to the art of imaging and more specifically to an improved xerographic system.

In a xerographic process, as described in U.S. Patent 2,297,691, a base plate of relatively low electrical resistance such as metal, paper, etc., having a photoconductive insulating surface thereon is electrostatically charged in the dark. The charged coating is then exposed to a light image. The charges leak off rapidly to the base plate in proportion to the intensity to the light to which any given area is exposed. After such exposure, the coating is contacted with electrostatic marking particles in the dark. These particles adhere to the areas where the electrostatic charges remain forming a powder image corresponding to the electrostatic image. The powder image can then be transferred to a sheet of transfer material resulting in a positive or negative print, as the case may be, having excellent detail and quality. Alternatively, where the base plate is relatively inexpensive, as of paper, it may be desirable to fix the powder image directly to the plate itself.

It has been previously known that certain inorganic films such as metallic oxides and sulfides have inherent photoconductive properties which make them useful in electrostatic processes. However, as a result of various limitations, it has been found that the usefulness of these pigments in electrostatic processes have been somewhat curtailed. For example, due to the conducting properties of the inorganic photoconductive pigments, it was found necessary to combine the pigments with a suitable binder insulating material in order to take advantage of their photoconductive properties. Furthermore, while it has been known that compounds of the Group III–V members of the Periodic Table also possess limited photoconductive properties, due to certain inherent characteristics, the use of these materials in electrophotography has been generally avoided.

While basically some of the above mentioned inorganic materials have been found useful under particular circumstances, such as in a binder system, in electrophotographic processes, there are inherent disadvantages to their use. One disadvantage, for example, is that spectral response over most of the light visible region cannot generally be obtained without resorting to additional treatments of the photoconductors. A second disadvantage to the use of the above-mentioned materials for xerographic plates is that any additonal treatment of the photoconductive materials is substantially limited by the agents which may be used effectively to give the desired results.

That is, if it is necessary to increase the spectral response of these photoconductive materials, such as by treatment with a doping agent, this can effectively be accomplished only with a very restricted number of dopants. As a result of the relatively high initial impurity content and substantial stoichiometric instability of the useful prior art photosensitive compounds the number of dopants or activating agents that may be utilized to affect a change in the electrophotographic properties of these compounds is substantially limited. Furthermore, due to these inherent properties, it is extremely difficult to control and predict the results which will be obtained when treating these compounds with these activating agents that are effective. A further disadvantage is that the above-mentioned stoichiometric instability significantly affects the electrical and optical properties of the photoconductive material. Still a further disadvantage of the above photoconductive materials is that they are limited by the type of charge to which they may be exposed when used in a xerographic mode.

It is therefore an object of this invention to provide a xerographic plate to overcome the above noted disadvantages.

It is a further object of this invention to provide a process of using a novel xerographic plate.

Another object of this invention is to provide a novel xerographic plate wherein spectral response can be obtained over most of the light visible region without resorting to further treatment of the photoconductive material.

Still a further object of this invention is to provide a novel xerographic plate wherein subsequent treatment of the photoconductive materials is not limited by the agents which may be used effectively to give the desired results.

Yet, still a further object of this invention is to provide a novel xerographic plate wherein the stability of the plate is not reduced by the photoconductive material utilized to make the plate.

An additional object of this invention is to provide a method of preparing a novel xerographic plate wherein the materials used to make the plate do not require the presence of a binder system.

Still an additional object of this invention is to provide a method of preparing a novel xerographic plate wherein the materials used to make the plate are not limited by the steps of the process, such as the type of charging required.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a xerographic plate prepared by depositing on the surface of a suitable substrate a homogeneous layer of photoconductive insulating material having a resistivity of at least 10^{12} ohms-cm. The photoconductive materials of this invention, gallium phosphide, aluminum phosphide, boron phosphide and mixtures thereof are doped at a temperature of about 1,000° C., preferably with oxygen or copper, either during the process of deposition or subsequent thereto, in order to raise the resistivity of the material to at least 10^{12} ohms-cm. The oxygen and copper dopants are preferred in order to achieve optimum results. As a result of the stoichiometric stability of the resulting photoconductive crystalline films deposited, it has been found that the elements of the compounds produced are, as closely as can be determined, combined in about a one to one ratio. It has further been found that as a result of these properties a xerographic plate of superior quality can be produced, specifically with regard to plate sensitivity and spectral response. It has been determined that when the photoconductive insulating materials of this invention are treated with an activator or dopant in such a manner as to raise their resistivities to at least 10^{12} ohms-cm. that these com-

pounds are useful for xerographic purposes. The resulting film coated substrate is suitable for use as a xerographic plate. It is to be noted that the xerographic plate of this invention is substantially a binderless plate, that is, the photoconductive insulating layer is a homogeneous crystalline film which does not require the presence of an insulating binder material. It is preferred, to obtain optimum results, that the photoconductive insulating layer contain at least about 80% of the activated photoconductive insulating material of the invention. The base substrate upon which the film is deposited is one which offers a relatively lower electrical resistance than the film itself and which will withstand the environmental conditions of the deposition system, such as selective metals, or other suitable material as more fully described hereafter. The film can be electrostatically charged and imaged in accordance with the conventional imaging process as described in U.S. Patent 2,297,691.

It is generally considered that the inorganic photoconductive films known to have utility for electrophotographic purposes, such as those disclosed in U.S. Patent 2,844,543 are limited in their application due to their restrictive insulating properties. Furthermore, the spectral response of these materials cannot ordinarily be attained over most of the light visible regions without resorting to additional treatment of the photoconductive materials. The photoconductive materials of the present invention are suitable for use when it is desirable to utilize light sources covering most of the light visible regions without resorting to further treatment of the photoconductive materials, therefore demonstrating panchromatic properties. Furthermore, although it is considered possible to extend the spectral response of the inorganic photoconductive materials presently found useful for electrostatic purposes by additional treatments with activating agents, it has been found that these materials can only be treated effectively by very limited number of such agents. As a result of the relatively high initial impurity content and substantial stoichiometric instability of the useful prior art photosensitive compounds the number of dopants or activating agents that may be utilized to affect a change in the electrophotographic properties of these compounds is substantially limited. Furthermore, due to these inherent properties, it is extremely difficult to control and predict the results which will be obtained when treating these compounds with these activating agents found to be effective. It has further been found that added treatments of the photoconductive insulating materials of this invention are not so limited. It is possible to dope gallium phosphide, aluminum phosphide, boron phosphide and mixtures thereof, with a greater variety of dopants as a result of the low impurity content and stoichiometric stability of these compounds. If it is found that difficulty develops when utilizing one specific dopant or activating agent then it is possible to readily substitute another equally effective but non-detrimental dopant. It has still further been found that the photoconductive insulating materials used in the course of this invention are much more controllable compounds than the photoconductive materials previously used. That is, they are not affected by stoichiometric deviations when prepared and therefore do not suffer from electrical and optical deviations, which is usually the case when employing the inorganic photoconductive materials previously found useful xerographically due to their well known unstable characteristics. It has also been determined that the photoconductive insulating materials of this invention can be prepared having either p-type or n-type conductivity, properties which are more fully described in U.S. Patent 3,041,166. A material is referred to as being of p-type when the majority charge carriers are holes and n-type when the majority charge carriers are electrons. Furthermore, the amphoteric properties of the photoconductive insulating materials of this invention lend flexibility to the system such as in the type of charging required.

In accordance with this invention, it has been found that a xerographic plate can be prepared by depositing on the surface of a suitable substrate a homogeneous layer of a high resistance photoconductive insulating material of the Group III–V compounds. More specifically, when homogeneous crystalline films of gallium phosphide, aluminum phosphide, boron phosphide, and mixtures of these compounds are deposited on the surface of a suitable substrate in such a manner so as to effect a resistivity increase to at least 10^{12} ohms-cm., it has been found that these compounds are quite useful for xerographic purposes. Ideally, the photoconductive materials of this invention should be near perfect insulators in the dark. In practice, material with a resistivity of at least 10^{12} ohms-cm. is preferred in order to obtain optimum results. However, material which has a resistivity of at least 10^{10} ohms-cm. when exposed to light are considered satisfactory.

The high resistivity photoconductive insulating materials of this invention are prepared by a vapor transport process whereby the photoconductive films are deposited on the surface of a suitable substrate. A purified dry hydrogen carrier gas is bubbled through a phosphorous containing component such as phosphorous trichloride maintained at a controlled temperature, approximately 0° C., and then passed over either gallium, aluminum or boron, the latter being maintained at a temperature between about 950–1,050° C. A reaction takes place in the presence of the metal, and the product is then swept down a temperature gradient to about 750–850° C. to be deposited on a suitable substrate in the form of a phosphide film of the respective metal. By introducing controlled amounts of a dopant, such as oxygen or copper, by way of the carrier gas, either during the process of deposition or subsequent thereto, the resistivity of the photoconductive film can be raised to at least 10^{12} ohms-cm. so that the resulting film will support an electrostatic charge in the dark. When oxygen is used as the doping agent, it may be supplied in a controlled manner by bubbling the hydrogen carrier gas through water at known temperatures, generally under ambient conditions. From the amount of water vapor incorporated in the gas stream, the concentration of the oxygen can be regulated. The amount of dopant required to raise the resistivity to the desired level will vary depending upon the impurity content initially present in the photoconductive material. Therefore, the amount of dopant required will be dependent upon the properties of the photoconductive film. A preferred range of the resistivity of the photoconductive film is between about 10^{12}–10^{15} ohms-cm. to produce optimum results. Any other suitable means may be used to raise the resistivity of these materials to the required critical value such as preferential removal of impurities from the photoconductive layer. However, the doping technique is preferred inasmuch as it is considered less critical, for example, than the purification process.

In addition to the above-mentioned photoconductive materials of this invention, any suitable combination of the Group III–V compounds may be treated in the manner herein described in order to achieve the required resistivity, if the combination is such that it has a band gap potential of at least 1.7 ov. or higher. A typical such photoconductive material is gallium arsenide phosphide. Above this potential, it has been found that the required dark resistivity of the photoconductive material can be obtained.

Although the spectral response obtained when using the photoconductive materials of this invention can be varied depending upon its desired results, it has been found that the preferred spectral range was determined to be in the visible spectrum, that is, from about 4,000 to 7,000 A.

Thickness of the photoconductive insulating film of the instant invention is not critical and may vary from about 1 micron to over 200 microns. When used, for example, in the process of electroradiography described

in U.S. Patent 2,666,144, the photoconductive film may be substantially thicker than 200 microns. However, in the present system it is preferred that the films be from about 20 to about 115 microns thick in order to obtain the maximum efficiency of the electrophotographic plate.

Any material suitable to raise the resistivity of the photoconductive insulating material of this invention to at least 10^{10} ohms-cm., preferably about 10^{12} ohms-cm., may be used in the course of this invention. Typical such doping agents are copper, silver, iron, cobalt, nickel, chromium, gold, manganese, oxygen, and mixtures thereof. Generally, the oxygen and copper doping agents are preferred inasmuch as the desired resistivity of the photoconductive film is more readily obtained.

Any suitable backing material for the xerographic plate may be used in the course of this invention. Generally, the preferred backing material should have an electrical resistance less than the photoconductive layer so that it may act as a ground when the film is electrostatically charged. Furthermore, the substrate upon which the photoconductive film is deposited must be such that it will withstand the conditions of the system in which the deposition is carried out. Typical such materials are brass, high melting point glass, steel, nickel, bronze, copper and engraver's copper and mixtures thereof. Other materials having electrical resistances and physical properties similar to the aforementioned can also be used as backing material to receive the photoconductive layer thereon. Other non-conductive materials capable of withstanding the environmental conditions of the present system may be used as the backing for the xerographic plate. When used, however, it is necessary to charge both sides of the xerographic plate according to the process set out in U.S. Patent No. 2,922,883.

The invention is illustrated in the accompanying drawing in which:

FIG. 1 is a side sectional view of an exemplary xerographic processing apparatus employing the improved plate of this invention;

FIG. 2 is a side view of the improved xerographic plate of this invention.

An exemplary xerographic copying apparatus adapted to employ the xerographic plate of this invention in the form of a cylindrical drum is shown in FIG. 1. The drum, when in operation, is generally rotated at a uniform velocity in the direction indicated by the arrow in FIG. 1 so after portions of the drum periphery pass the charging unit **18** and have been uniformly charged, they come beneath a projector **19** or other means for exposing the charged plate to the image to be reproduced. Subsequent to charging and exposure, sections of the drum surface move past the developing unit, generally designated **21**. This developing unit is of the cascade type which includes an outer container or cover **22** with a troph at the bottom containing a supply of developing material **23**. The developing material is picked up from the bottom of the container and dumped and cascaded over the drum surface by a number of buckets **24** on an endless driven conveyor belt **26**. This development technique, which is more fully described in U.S. Patents 2,618,552 and 2,618,551 utilizes a two element development mixture including finely divided, color marking particles or toner and larger carrier beads. The carrier beads serve both to deagglomerate, the fine toner particles for easier feeding, and charge them by virtue of the relative positions of the toner and carrier material in the triboelectric series. The carrier beads with toner particles clinging to them are cascaded over the drum surface. The electrostatic field from the charge pattern on the drum pulls toner particles off the carrier beads serving to develop the image. The carrier beads, along with any toner particles not used to develop the image, then fall back into the bottom of container **22** and the developed image moves around until it comes into contact with the copy web **27** which is passed up against the drum surface by two idler rollers **28** so that the web moves at the same speed as the periphery of the drum. The toner in the developing mixture is periodically replenished from a toner dispenser not shown. A transfer unit **29** is placed behind the web and spaced slightly from it between the rollers **28**. This unit is similar in nature to the plate charging mechanism **18** in that both operate on the corona discharge principle. Both the charging device **18** and the transfer unit **29** are connected to a source of high D.C. potential of the same polarity identified as **31** and **32**, respectively, and including a corona discharge wire **33** and **34**, respectively, surrounded by a conductive metal shield.

In the case of charging unit **18**, voltage source **31** is preselected to be of such a magnitude that it will produce a corona discharge on the drum under almost any conditions of relative humidity and atmosphere pressure normally encountered which would tend to charge a conventional xerographic plate well above the desired voltage. This "excessively" high potential source is preset and need not be adjusted because the retained voltage on the plate is controlled by the electrical characteristics of the plate itself in such a way that any excessive current which flows through the plate during the corona discharge is drained away by the voltage regulating characteristics of the plate. In the case of the corona discharge transfer unit, a charge is deposited on the back of web **27** and this charge is of the same polarity as the charge initially deposited on the drum and also opposite in polarity to the toner particles utilized in developing the drum. The discharge deposit on the back of web **27** pulls the toner particles away from the drum by overcoming the force of attraction between the particles and the charge on the drum. It should be noted at this point that many other transfer techniques can be utilized in conjunction with the invention. For example, a roller connected to a high potential source opposite in polarity to the toner particles may be placed immediately behind the copy web or the copy web itself may be adhesive to the toner particles. After transfer of the toner image to web **27**, the web moves beneath a fixing unit **36** which serves to fuse or permanently fix the toner image to web **27**. In this case, a resistance heating-type fixer is illustrated. However, here again, other techniques known in the art may also be utilized including the subjection of the toner image to a solvent vapor or spraying of the toner image with an adhesive film forming overcoating. After fixing, the web is rewound on a coil **37** for later use. After passing the transfer station, the drum continues around and moves beneath the cleaning brush **38** which prepares it for a new cycle of operation. It should be noted that this apparatus may also be operated at varying speeds by setting the corona discharge unit at a high enough voltage so that the plate will be charged fully at the highest speed. Then, overcharging will not occur at the lower speeds because of self-regulation by the plate.

Although the invention has been described in connection with corona charging, it is to be understood that this is exemplary only, and that the self-regulating plate may, in fact, be employed with any suitable charging technique. Other typical charging methods include friction charging and induction charging as described in U.S. Patents 2,934,649 and 2,833,930 and roller charging as described in U.S. Patent 2,934,650.

FIG. 2 illustrates a xerographic plate **10** comprising backing material **11** and a photoconductive insulating layer **12**. The selection of the supporting substrate layer **11** is based upon the desired use of the xerographic plate, such as to give the plate additional strength or to provide added flexibility in situations requiring it.

To further define the specifics of the present invention, the following examples are intended to illustrate and not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated. The examples are also to illustrate various preferred embodiments of the present invention.

EXAMPLE I

Pure dry hydrogen, delivered by a palladium diffusion purifier, is bubbled through phosphorous trichloride maintained at a temperature of about 0° C. and then passed over gallium at about 1,000° C. A controlled amount of oxygen, approximately less than 100 parts per million, is introduced into the system by bubbling the hydrogen carrier gas through water maintained at ambient conditions. The water vapor incorporated into the gas stream supplies the required oxygen concentration. The reaction product of the phosphorous trichloride vapors and gallium vapors, gallium phosphide, is swept down a temperature gradient to about 800° C. where it is deposited upon an aluminum substrate as a thin homogeneous layer about 100 microns thick. The amount of the doping agent introduced is controlled so as to increase the resistivity of the photoconductive film to at least about 10^{12} ohms-cm. The resulting film coated plate is then charged to about 350–400 volts by means of a laboratory corotron unit powered by high voltage power supply. The charging current is 0.1 of a milliamp at 7,500 volts. A transparent positive USAF test chart is placed on the charged gallium phosphide plate and exposed with a 75-watt photoflood lamp. An exposure of about 100 foot-candle-seconds is required for the gallium phosphide plate. The electrostatic latent image produced is then developed with electrostatic marking particles or toner.

EXAMPLE II

The procedure of Example I is repeated excepting aluminum is substituted for gallium, thereby resulting in the deposition on the aluminum substrate a doped aluminum phosphide film in place of the gallium phosphide film of Example I. The resulting xerographic plate has a dark decay rate slightly less than the plate of Example I.

EXAMPLE III

The procedure of Example I is repeated excepting boron is substituted for gallium, thereby resulting in the deposition on the aluminum substrate a doped boron phosphide film in place of the gallium phosphide film of Example I. The resulting xerographic plate has a slightly higher decay rate in the dark as compared to the gallium phosphide plate.

EXAMPLE IV

The procedure of Example I is repeated excepting a mixture of aluminum and gallium is substituted for the gallium, thereby resulting in the deposition on the aluminum substrate of a doped film comprising aluminum phosphide and boron phosphide. The resulting xerographic plate has a dark decay rate comparable to that of Example II.

Although the present examples were very specific in the terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to prepare the xerographic plate of the present invention, other steps or modifications may be used if desirable, such as in the technique of doping or in the manner of contacting the reactants. While it is preferred, in order to obtain optimum results, that the photoconductive layer of the plate contain at least about 80% of the inorganic photoconductive composition, other materials may be incorporated in the xerographic plate of this invention which will enhance, synergize, or otherwise desirably effect the properties of the materials presently used. For example, the spectral sensitivity of the plate in accordance with the instant invention may be modified through the inclusion of photosensitizing dyes therein.

Anyone skilled in the art will have other modifications occur to him based on the teaching of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A xerographic plate comprising a supporting substrate having on one side thereof a photoconductive insulating layer in the form of a substantially homogeneous crystalline film, said substrate having an electrical resistance less than said photoconductive layer, said photoconductive layer comprising at least about 80 percent of an inorganic photoconductor composition selected from the group consisting of gallium phosphide, aluminum phosphide, boron phosphide and mixtures thereof, said composition having a resistivity of at least 10^{10} ohm-cm.

2. A xerographic plate capable of forming an electrostatic image developable with electrostatic marking material comprising a supporting substrate having at least one member selected from the group consisting of steel, nickel, high melting point glass, and copper, having on one surface thereof a photoconductive insulating layer in the form of a substantially homogeneous crystalline film, said substrate having an electrical resistance less than the photoconductive layer, such photoconductive insulating layer comprising at least about 80 percent of an inorganic photoconductor composition selected from the group consisting of gallium phosphide, aluminum phosphide, boron phosphide and mixtures thereof, said composition having a resistivity of at least about 10^{10} ohm-cm.

3. A xerographic plate according to claim 2 in which the supporting substrate is nickel, and said inorganic photoconductor composition comprises gallium phosphide.

4. A xerographic plate according to claim 2 in which the supporting substrate is nickel and said inorganic photoconductor composition comprises aluminum phosphide.

5. A xerographic plate according to claim 2 in which the supporting substrate is nickel and said inorganic photoconductor composition comprises boron phosphide.

6. A xerographic plate as defined in claim 2 in which the supporting substrate comprises nickel and said inorganic photoconductor composition comprises a mixture of gallium phosphide and aluminum phosphide.

7. A xerographic plate comprising a supporting substrate having on one surface thereof a photoconductive insulating layer in the form of a substantially homogeneous crystalline film comprising at least one phosphide compound formed with a Group III element, said substrate having an electrical resistance less than said photoconductive insulating layer, said photoconductive insulating layer having a resisitivity of at least 10^{10} ohm-cm. and being capable of supporting an electrostatic charge in the dark and dissipating a portion of said charge in response to electromagnetic radiation impinging thereon.

8. A method of producing electrostatic charge pattern which comprises applying an electrostatic charge to a photoconductive insulating film comprising a substantially homogeneous crystalline film selected from the group consisting of gallium phosphide, aluminum phosphide, boron phosphide, and mixtures thereof, said inorganic photoconductor composition having a resistivity of at least 10^{10} ohm-cm. and exposing said charged layer to a pattern of activating electromagnetic radiation to form an electrostatic image.

9. A process of producing an electrostatic image corresponding to a pattern of light and shadow which comprises applying an electrostatic charge pattern to the surface of a xerographic plate, said plate comprising a supporting substrate having at least one member selected from the group consisting of steel, nickel, high melting point glass and copper, said substrate having on one surface thereof a photoconductive insulating layer in the form of a substantially homogeneous crystalline film, said substrate having an electrical resistance less than the photoconductive layer, said photoconductive layer comprising at least about 80 percent of an inorganic photoconductor composition selected from the group consisting of gallium phosphide, boron phosphide and mixtures

thereof, said composition having a resistivity of at least 10^{10} ohm-cm., exposing the electrostatically charged surface to a pattern of light and shadows so that an electrostatic latent image is formed corresponding to said pattern, and depositing electrically attractable marking materials selectively in conformity with the electrostatic image thus produced.

10. A process according to claim **9** in which the cycle of charging, exposing, and developing the image is repeated at least twice.

11. A process for producing a xerographic reproduction comprising placing an electrostatic charge on a photoconductive insulating surface of a xerographic member comprising an electrically conductive backing member having thereon a photoconductive insulating layer in the form of a substantially homogeneous crystalline film, said crystalline film comprising at least one phosphide compound formed with a Group III element, and said film having a resistivity of at least 10^{10} ohm-cm. and being capable of supporting an electrostatic charge in the dark and dissipating a portion of said charge in response to electromagnetic radiation impinging thereon; selectively dissipating a portion of said electrostatic charge from the surface of the charged photoconductive insulating layer by exposing the charged layer to a light image, thereby creating a latent electrostatic image on the surface of the insulating layer; and developing said latent electrostatic image with electroscopic marking material.

12. A process for preparing a xerographic plate which comprises mixing under reaction conditions in the presence of an activator selected from the group consisting of copper, silver, gold, iron, nickel, and oxygen and mixtures thereof, a phosphorus trichloride vapor and the vaporized state of gallium, said reaction being carried out at a temperature range of about 950–1,050° C. and at a pressure of about one atmosphere, to affect the formation of gallium phosphide vapor, and condensing said gallium phosphide vapor on the surface of a receiving substrate in the form of a crystalline film, said film having a resistivity of at least 10^{10} ohm-cm., with said substrate being maintained at a temperature sufficiently low to allow for the formation of said crystalline film.

13. The process of claim **12** in which the activator comprises oxygen and said substrate comprises nickel.

14. The process of claim **12** in which the activator comprises copper and said substrate comprises nickel.

15. The process of claim **12** in which said crystalline film comprises about 80 percent of said condensed gallium phosphide.

References Cited

UNITED STATES PATENTS

2,938,816	5/1960	Gunther	252—501 X
3,043,958	7/1962	Diemer	252—501 X
3,121,006	2/1964	Middleton et al.	96—1.5 X
3,261,080	7/1966	Grimmeiss et al.	252—501 X

GEORGE F. LESMES, Primary Examiner

C. E. VAN HORN, Assistant Examiner

U.S. Cl. X.R.

23—105; 96—1; 117—106, 127, 230; 252—501