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PHOTOSENSITIVE INSULATING MATERIAL

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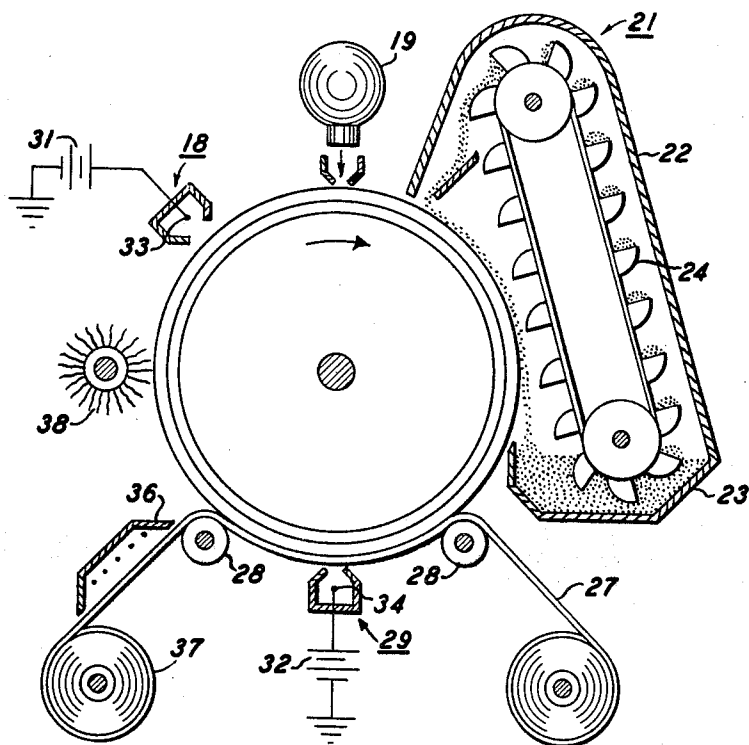


FIG. 1

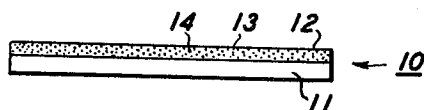


FIG. 2

INVENTORS
 CHARLES WOOD
 G. SANJIV KAMATH
 BY JAMES H. NEYHART
James J. Kales
Stanley Z. Role
 ATTORNEYS

1

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PHOTOSENSITIVE INSULATING MATERIAL

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

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ABSTRACT OF THE DISCLOSURE

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

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

In the xerographic process as described in U.S. Pat. 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 of 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 photoconductors in a binder system have utility for xerographic purposes. For example, it is known to use an inorganic photoconductive pigment in a non-photoconductive resin binder for xerographic purposes and it is further known to use the same inorganic pigments in a photoconductive binder. 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 certain circumstances in electrophotographic processes, it has been found that 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 additional 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 nec-

2

essary to increase the spectral response of these photoconductive materials, such as by treatment with a doping agent, this can be effectively accomplished only with a very restricted number of dopants. As a result of the relatively high starting 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 with the effective activating agents. A further disadvantage is that the above-mentioned instability significantly affects the electrical and optical properties of the photoconductive material. Still a further disadvantage of the above-mentioned 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 which will 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 attained 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 dependent upon 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 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 intimately mixing and grinding together a photoconductive insulating material in a high electrical resistance binder. The photoconductive materials of this invention, gallium phosphide, gallium arsenide phosphide, aluminum phosphide, boron phosphide, and mixtures thereof, prepared by the well-known vapor transport process are doped at a temperature of about $1,000^{\circ}$ C., preferably with oxygen or copper, prior to mixing with the resinous binder solution, in order to raise the resistivity of the material to at least 10^{10} ohms-cm. The oxygen and copper dopants are preferred in order to achieve optimum results. The preferred blend of the photoconductive insulating material with the binder solution is about 1-2 parts of the photoconductive material per about 5-1 part binder solution, by volume. It has been found that these proportions produce a plate of superior xerographic properties, specifically with regards to plate sensitivity and spectral response. It has been found that when the photoconductive insulating materials of this invention are treated with an activator or dopant in such a manner so as to raise their resistivities to at least 10^{10} ohms-cm., and then blended with the appropriate high electrical resistance binder that these compounds are useful for xerographic purposes. The resulting mixture is suitable as the photoconductive insulating layer of the xerographic plate and may be coated on any suitable support material offering a relatively lower electrical resistance than the coating such as metal, paper, or suit-

able plastics as more fully described hereafter. The coating can be electrostatically charged and imaged in accordance with the conventional xerographic imaging process as described in U.S. Pat. 2,297,691.

It is generally considered that the inorganic photoconductors known to have utility for xerographic purposes such as those disclosed in U.S. Pats. 3,121,006 and 3,121,007 are limited in their application inasmuch as the spectral response of these materials can not ordinarily be attained over most of the light visible regions without resorting to additional treatments 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 material, therefore demonstrating panchromatic properties. Furthermore, although it is considered possible to extend the spectral response of the inorganic photoconductors presently found useful for xerographic purposes by additional treatments with activating agents, it has been found that these photoconductive materials can only be treated effectively by a limited number of such agents. As a result of the relatively high initial impurity content and substantial stoichiometric instability of the useful prior art photoconductive compounds, the number of dopants or activating agents 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 with the effective activating agents. 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 the Group III-V compounds 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 those 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. Pat. 3,041,166. A material is referred to as being of the p-type when the majority charged carriers are holes and n-type when the majority charged 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 intimately mixing together high resistance photoconductive insulating material of the Group III-V compounds with a high electrical resistance binder. More specifically, when gallium phosphide, gallium arsenide phosphide, aluminum phosphide, boron phosphide and mixtures of these compounds are treated in such a manner so as to effect a resistivity increase to at least 10^{10} ohms-cm. it has been found that these materials when combined with suitable binder materials are quite useful for xerographic purposes. The binder material which is employed in cooperation with the photoactive compounds is a material which is an insulator to the extent that an electrostatic charge placed on the layer is not conducted by the binder at a rate to prevent the formation and retention of an electro-

static latent image thereon. Furthermore, the binders should not react chemically with the photoactive compound. The binder material adheres tightly to the base material and provides an efficient dispersing medium for the photoactive particles.

The high resistivity photoconductive insulating material of this invention is prepared by controlled doping of the photoactive material at a temperature of at least about 800° C. until the resistivity of the photoconductive insulating material is raised to at least 10^{10} ohm-cm. so that when combined with the binding material the uniform photoconductive insulating layer will support an electrostatic charge in the dark. The upper temperature limit of the doping step is limited only by the requirements of the system. The preferred range of the resistivity of the photoconductor is between about 10^{10} - 10^{15} ohm-cm. to produce optimum results. Any other suitable means may be used to raise the resistivity of these compounds 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 less critical, for example, than the purification process.

The doped photoconductive insulating material is reduced to a powdered form by grinding together in a ball mill or other suitable means until the size of the particles are sufficiently small so that they will not destroy the insulating effect of the binder material mixed therewith. For maximum efficiency, it is preferred that the particle size of the photoconductive material be at least 200 mesh or smaller. The finely divided particles are then blended in the presence of a suitable solvent with a binder resin and mixed thoroughly until a viscous paste-like texture is obtained. It is only essential that enough solvent be present during milling to give good grinding viscosity. The paste is then applied to the surface of a base plate in a thin uniform layer by any suitable means such as with a brush, draw blade, by dipping, or by roller coating. At the end of the milling period, additional solvent may be added and stirred into the mixture sufficient to render it sprayable. The resulting composition can then readily be sprayed at room temperature onto a clean base plate.

The base substrate bearing the photoconductive insulated layer is then dried at a temperature sufficient to cause complete evaporation of the solvent from the binder composition without destroying the stability of the binder resin. After the solvent has evaporated from the composition, the coating can be electrostatically charged and used in the electrophotographic or xerographic process. Although the spectral response obtained when using the photoconductive materials of the invention can be varied depending upon the 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 Å.

Thickness of the photoconductive insulating layer 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. Pat. 2,666,144, the photoconductive layer may be substantially thicker than 200 microns. However, in the present system, it is preferred that the photoconductive layers be from about 20 to 115 microns thick in order to obtain the maximum efficiency of the electrophotographic plate.

In general, the ratio between binder and the inorganic photoconductive insulating compound is from about 1 part binder and 10 parts photoconductive to about 2 parts binder and 1 part photoconductor by volume. The preferred blend is from about 1-2 parts photoconductor to about 5-1 parts binder to produce a xerographic plate of maximum efficiency. The actual proportion will, of course, depend upon the specific binder as well as on the properties and characteristics desired. As a general guide, it is indicated that the quantities of the binder would be the least amount which will adequately secure the

photoconductor to the surface of the backing member and which will form a smooth and useful surface for the ultimate deposition thereon of electrostatically charged powder particles.

Any suitable binder material may be used in the course of this invention. Typical such binder materials are those disclosed in U.S. Pats. 3,121,006 and 3,121,007. While the nature of the binder material is not critical it does have a definite effect upon the light sensitivity of the composite layer. In general, those binders having strongly polar groups such as carboxyl groups, chloride, etc. are preferred over the straight hydrocarbon binders. It is believed that injection of carriers from the photoconductor to the binder is facilitated through the presence of such groupings and further that the bonding of the photoactive compounds to the binder is improved thereby. Examples of such binder resins are polymerized butyl methacrylates, polyvinyl chloride, polyvinyl acetate, polyacrylic acid esters, and vinyl chloride-vinyl acetate copolymers. In addition, other suitable binder materials are charge-transfer type photoconductive materials such as disclosed in applications, Ser. Nos. 426,409; 426,423; 426,428; 426,431 and 426,396, filed in the U.S. Patent Office on Jan. 18, 1965.

Any suitable solvent may be used in the course of this invention. The solvent used should be such as to readily evaporate and be a substantially pure, organic, low boiling-point hydrocarbon solvent and should not introduce impurities which would lower electrical resistance of the coating. Typical such solvents are toluene, ethylene glycol monoethyl ether acetate, xylene, benzene, methyl isobutyl ketone, or mixtures thereof. Preferred solvents used in the instant invention are benzene, xylene, toluene, and methyl isobutyl ketone inasmuch as they have been found to give the most satisfactory results.

Any material suitable to raise the resistivity of the photoconductive insulating material of the invention to at least about 10^{10} ohm-cm. may be used in the course of this invention. Typical such doping materials are copper, silver, iron, cobalt, gold, manganese, chromium, nickel, oxygen, and mixtures thereof. Generally, the oxygen and copper doping agents are preferred inasmuch as the desired resistivity of the photoconductive insulating material 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 will act as a ground when the film is electrostatically charged. Typical such materials are aluminum, brass, glass, aluminum coated glass, steel, nickel, bronze, copper, engraver's copper, engraver's zinc, grained lithographic zinc, and paper. Other materials having electrical resistances similar to the aforementioned can also be used as backing material to receive the photoconductive layer thereon. Other nonconductive materials such as thermoplastics 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. Pat. 2,922,883.

The invention is illustrated in the accompanying drawings 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 trough at the bottom containing a supply of developing material 23. The developing material is picked up from the bottom of the container and dumped or 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. Pats. 2,618,552 and 2,618,551, utilizes a two element development mixture including finely divided, colored 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 a copy web 27 which is passed up against the drum surface by two idle rollers 28 so that the web moves at the same speed as is 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 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 conductive metal shield. In the case of charging unit 18, voltage source 31 is preselected to be of such a magnitude that it would produce a corona discharge on the drum under almost any conditions of relative humidity and atmospheric pressure normally encountered which would tend to charge a conventional xerographic plate well above the desired voltage. This "excessively" high potential source is pre-set 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, 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. A 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 difficult charging methods include friction charging and induction charging as described in U.S. Pats. 2,934,649 and 2,833,930 and roller charging as described in U.S. Pat. 2,934,650.

FIG. 2 illustrates a xerographic plate 10 comprising backing material 11 and a photoconductive insulating layer 12 comprising a binder material 13 and inorganic photoconductive material 14. 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 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 also illustrate various preferred embodiments of the present invention.

EXAMPLE I

Gallium phosphide crystals prepared by the well known vapor transport process are doped in an atmosphere of hydrogen carrier gas and water vapor until the resistivity of the crystals is raised to at least 10^{10} ohm-cm. The reaction zone is maintained at a temperature of about $1,000^{\circ}$ C. and at a pressure of about 1 atmosphere. A controlled amount of oxygen dopant, approximately less than 100 p.p.m., is introduced by way of the carrier gas-water system. The resulting gallium phosphide crystals are then ground in a ball mill until the crystals are reduced to about 300 mesh powder. A binder mixture comprising Lucite, a polymerized butyl methacrylate available from E. I. du Pont de Nemours & Co., in xylene, about 11–20 percent by weight, is prepared and blended with the gallium phosphide powder, 1 gram of powder per 1 ml. of binder solution. The binder composition is thoroughly mixed with the gallium phosphide powder to a viscous paste. The paste is then coated onto an aluminum conductive substrate in a thin uniform layer about 100 microns thick. The resulting coated substrate is then heated to a temperature of about 150° C. in order to dry the photoconductive layer and expedite the evaporation of the solvent present. The resulting electrophotographic plate is charged to about 350–400 volts by means of a laboratory Corotron unit powered by a 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 doped gallium arsenide phosphide crystals of a resistivity of at least 10^{10} ohm-cm. are substituted for the doped gallium phosphide crystals. The resulting xerographic plate has a slightly higher decay rate in the dark as compared to the gallium phosphide plate.

EXAMPLE III

The procedure of Example I is repeated excepting a doped mixture of gallium phosphide and gallium arsenide

phosphide crystals of a resistivity of at least 10^{10} ohm-cm. is substituted for the doped gallium phosphide crystals. The results obtained are similar to those of Example II.

EXAMPLE IV

The procedure of Example I is repeated excepting a doped mixture of gallium phosphide and aluminum phosphide crystals of a resistivity of at least 10^{10} ohm-cm. is substituted for the doped gallium phosphide crystals. The resulting xerographic plate has a dark decay rate slightly less than the plate of Example I.

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. In addition, other materials may be incorporated in the xerographic plate of this invention which will enhance, synergize, or otherwise desirably effect the properties of materials presently used. For example, the spectral sensitivity of plates prepared 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 surface thereof a photoconductive insulating layer, said substrate having an electrical resistance less than said photoconductive layer, said photoconductive layer comprising a resin binder and an inorganic photoconductor composition selected from the group consisting of gallium phosphide, gallium arsenide phosphide, aluminum phosphide, boron phosphide, and mixtures thereof, with said composition having a resistivity of at least 10^{10} ohm-cm.

2. The plate of claim 1 in which the resistivity of the compound has been increased by doping with an activator material selected from the group consisting of oxygen and copper.

3. A method of imaging which comprises applying an electrostatic charge to a photoconductive layer comprising a finely-divided inorganic photoconductor dispersed in a highly insulating resin binder, said inorganic photoconductor being selected from the group consisting of gallium phosphide, gallium arsenide phosphide, aluminum phosphide, boron phosphide, and mixtures thereof, said inorganic photoconductor having a resistivity of at least 10^{10} ohm-cm., and exposing said charged layer to a pattern of activating electromagnetic radiation to form a latent electrostatic image on the surface of said photoconductive layer.

4. The method of claim 3 in which the latent electrostatic image is developed with electroscopic marking material.

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GEORGE F. LESMES, Primary Examiner

C. E. VAN HORN, Assistant Examiner

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