

[54] **PHOTOCONDUCTIVE BODY FOR ELECTROPHOTOGRAPHY AND THE METHOD OF MANUFACTURING THE SAME**

[75] Inventors: **Hiroshi Hanada**, Yokohama; **Toru Takahashi**, Tokyo, both of Japan

[73] Assignee: **Canon Kabushiki Kaisha**, Tokyo, Japan

[22] Filed: **Mar. 4, 1969**

[21] Appl. No.: **804,142**

[30] **Foreign Application Priority Data**

Mar. 6, 1968 Japan..... 43-15287

[52] **U.S. Cl.**..... **96/1.5**; 96/1 R; 96/1 PS; 96/1.8; 148/33; 148/187; 148/188; 252/62.3 ZT; 252/501; 427/74; 427/85; 427/87; 428/323; 428/403

[51] **Int. Cl.²**..... **G03G 5/087**

[58] **Field of Search**..... 96/1.5, 1 R, 1 PS, 1.8; 117/100, 69, 100 B, 200, 215, 33.5 R, 35 S, 201; 252/501, 301.6 S, 62.3 ZT; 5/11; 29/572; 148/33, 187, 188

[56] **References Cited**

UNITED STATES PATENTS

2,844,640 7/1958 Reynolds 252/501
2,876,202 3/1959 Busanovich et al..... 252/501

2,908,588	10/1959	Harper.....	117/33.5
3,041,166	6/1962	Bardeen.....	117/200
3,060,134	10/1962	Elder.....	252/501
3,162,526	12/1964	Vanik.....	117/200
3,251,714	5/1966	Rotschild.....	117/201
3,307,983	3/1967	De Hann et al.....	117/200
3,312,547	4/1967	Levy.....	117/200
3,351,516	11/1967	Weisbeck et al.....	117/33.5 R
3,374,108	3/1968	Keramidas.....	117/200
3,379,527	4/1968	Corrsin et al.....	96/1.5
3,449,148	6/1969	Shortes.....	117/100 B
3,519,480	7/1970	Trautweiler.....	117/201
3,541,028	11/1970	Makino et al.....	252/301.6 S
3,560,398	2/1971	Shortes.....	252/301.6 S
3,568,306	3/1971	Yamashita.....	136/89
3,595,646	7/1971	Kinoshita.....	252/501

Primary Examiner—George F. Lesmes

Assistant Examiner—Charles E. Lipsey

Attorney, Agent, or Firm—Watson Leavenworth
Kelton & Taggart

[57] **ABSTRACT**

A photoconductive body for electrophotography and methods of manufacturing the same. The present invention provides a high sensitivity photoconductive powder of CdS or CdSe by activating powder particles with a surface treatment to provide a potential barrier susceptible to the light, to improve trap level of the surface of the particles and to increase the quantum efficiency of the particles.

25 Claims, 3 Drawing Figures

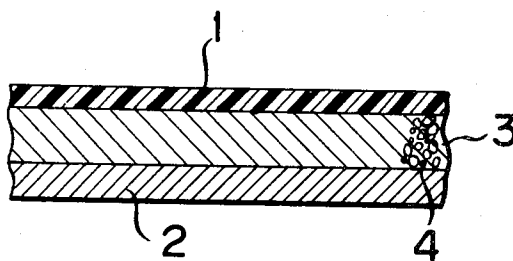


FIG. 1

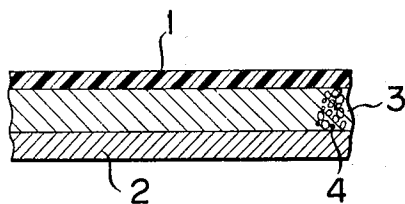


FIG. 2

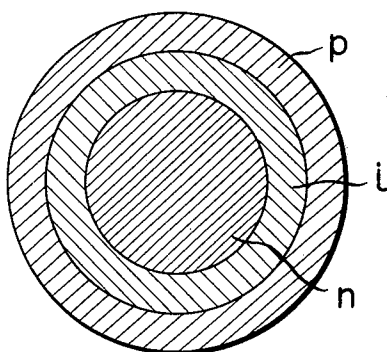
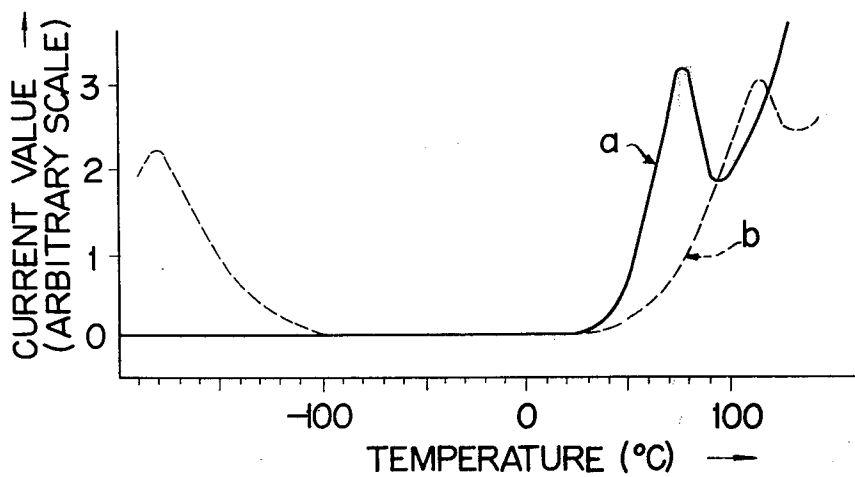


FIG. 3



PHOTOCONDUCTIVE BODY FOR ELECTROPHOTOGRAPHY AND THE METHOD OF MANUFACTURING THE SAME

This invention relates to a powdered photoconductive body for use in electrophotography, to a photosensitive plate for electronic photography using the said photoconductive body, and to methods of manufacturing the said photoconductive body.

An object of this invention is to obtain a high-sensitivity, high-resolution power, and highly durable electrophotographic photosensitive plate best suited for use in methods for electrophotography, particularly those described in U.S. applications Ser. Nos. 563,899 filed July 8, 1966 and 571,538 filed Aug. 10, 1966.

The above-mentioned methods for electrophotography feature the formation of a high contrast electrostatic image by applying a uniform primary electrical charge to the insulating surface of a photosensitive plate having a highly insulating layer in close adherence thereto, by removing the said charge by either applying an electrical charge opposite in polarity to that of the primary charge or by AC corona discharge simultaneously with an exposure, and then by illuminating the entire surface with light. This process is superior to the method known as the Carlson method in sensitivity, in durability of photosensitive plate for repeated use, and in economy. The photosensitive plate used in this process comprises a highly-insulating layer, a photoconductive layer, and an electrically conductive or insulating base. However, a photosensitive plate comprising four layers including one more insulating layer on a electrically conductive base, or a photosensitive plate including layers above and/or below the photoconductive layer transparent to radiation to which the photoconductive layer is sensitive, can also be used. The performance, such as image quality and sensitivity, is determined depending on the photoconductive material and plate structural condition.

In the conventional Carlson process, semiconductors such as amorphous selenium, which have a sufficiently high resistance, that is, have an insulation of more than $10^{12} \Omega\text{-cm}$ in darkness, are required in the photosensitive plate in order to maintain electrostatic charges on its surface. Therefore, highly sensitive layers having the distinct characteristic of a p-type semiconductor or an n-type semiconductor as a result of mixing highly sensitive photoconductive bodies such as CdS, CdSe, crystalline, Se, SeTe, Te or impurities and forming donors or acceptors, cannot be used practically because they have a large dark decay or attenuation.

In the above-mentioned novel process, however, the photosensitive plate has an insulating layer on its surface and, based on some internal physical phenomena not yet clear, such highly sensitive substances such as CdS and crystalline Se can be employed as the photoconductors, that is, mixing of impurities can be made with more freedom. This enables easier selection of p-type semiconductors and n-type semiconductors as sensitizing materials. In fact, photosensitive plates far superior in sensitivity to those of Carlson process can be obtained by using semiconductors of either type.

However, more-speedy and more-sensitive photosensitive plates are required at present. This invention was developed to meet this requirement.

In a photosensitive layer made by bonding pulverized photoconductive substance for electrophotography with

a resin the photoconductive characteristic is determined depending mainly on the potential barrier that exists on the surface of the powder granules and between the granules. Therefore, in order to obtain a highly sensitive photosensitive layer, such powder, whose granule surface potential barrier changes rapidly with incident light, must be used.

In a photosensitive plate of said three layer type or other general type used in electrophotography, the photoconductive characteristic is formed by the trapping of the exciting carriers as determined by the trap level within the photosensitive layer. Such trap level exists mostly on the surface of the powdered particles so that the suitable treatment of the surface of the particles would produce new trapping ability.

However, this matter is not taken into consideration in conventional methods for preparing powder of cadmium sulfide or cadmium selenide photoconductive substances, and the only known method is to make a semiconductor layer of copper suboxide in contact with the surface of powder granules of sulfides or selenide of cadmium in order to obtain a finer powder granule. This method does not give a highly sensitive photosensitive layer.

This invention attains the purpose of providing high sensitivity powder granules of sulfides or selenide or cadmium by activating the powder granules with a surface treatment by a novel method.

There are two known methods of increasing the sensitivity of photosensitive plate for electrophotography. One is to extend the range of sensitive wavelengths of sensitizing materials and the other is to increase the quantum efficiency of the photoconductivity. In sensitizing materials such as cadmium sulfide or cadmium selenide, photoconductive material, which inherently have sufficiently wide range of sensitive wavelengths, a drastic improvement in sensitivity cannot be expected by a further extension of the range of sensitive wavelengths. Therefore, increasing the sensitivity of a photosensitive layer containing powder granules of sulfides or selenide of cadmium should be considered along the line of increasing the quantum efficiency of photoconductivity.

However, the conventional ideas of quantum efficiency that have been applied to the so-called photoconductive cells that used monocrystals or sintered layers are not applicable to photosensitive plates for electrophotography, because the quantum efficiency of these photoconductive cells is measured by conducting photoelectric current into an external circuit through an electrode attached to the photoconductive cell, the electrode having a so-called ohmic contact, whereas in a photosensitive plate for electrophotography an electrode having an ohmic contact is not used and the quantum efficiency must be considered in the interior of the photosensitive layer. The conventional method to increase the life of the exciting carrier used in sensitizing the photoconductive cell results in a quantum efficiency of at most 1.

If, however, the carrier increasing mechanism known concerning the *n-p-n* hook phototransistor is considered, a drastic increase in the sensitivity of the photosensitive layer may be expected by applying the said mechanism to the photosensitive layer to increase the quantum efficiency of the photosensitive layer to a value for larger than 1.

The carrier increasing mechanism of the *n-p-n* hook transistor will be now explained. This is an *n-p-n* junction having a thin *p*-type layer between *n*-type layers. When an external voltage is applied to this junction, the *p-n* junction becomes, for example, forward biased and the *n-p* junction becomes reverse biased.

In this construction, the intermediate thin *p*-type layer serves as the so-called potential barrier to electrons. When rays of light within the sensitive-wavelength range impinge in the neighborhood of the *p*-type layer of this *n-p-n* construction, especially the neighborhood of the junction where reverse bias is being applied, as an electron-positive hole pair is excited, the positive hole and electron produced are separated from each other by the strong electric field of reverse bias, and the electron moves towards the *n*-type layer and the positive hole to the *p*-type layer. The positive hole that has moved towards the *p*-type layer is held by the valence bond of the *p*-type layer and maintained in that section.

The greater the number of positive holes separated, the more positive holes stored in the *p*-type layer and the potential barrier of the *p*-type layer is lowered by the positive valency of the positive holes. As a result, free electrons in the *n*-type layer on the forward biased side enter the *p*-type layer easily, disperse in the layer, and, when they reach the reverse biased side, flow immediately into the *n*-type layer on the opposite side by the strong electric field of the reverse bias.

This can be compared to the case of a dam. The *p*-type layer corresponds to the flood gate and the action by which the incident light sends positive holes into the *p*-type layer corresponds to opening the flood gate. As a result, more water flows out of the dam the larger the opening of the flood gate.

From the explanation given above it is clear that the carrier increasing mechanism of *n-p-n* hook gives a large quantum efficiency that exceeds 1. The quantum efficiency based on the known theory on the *n-p-n* hook is given by the following formula:

$$Y = 1 + (\sigma_e L_{pe} / \sigma_p w)$$

where, Y is quantum efficiency, σ_e the electroconductivity of the *n*-type layer on the forward bias side, L_{pe} the diffusion distance of positive holes within the said layer, σ_p the electroconductivity of the intermediate *p*-type layer, and w the thickness of the said layer. Therefore, when $\sigma_e L_{pe}$ is far greater than $\sigma_p w$, the quantum efficiency is far greater than 1.

An object of this invention is to increase the sensitivity of photosensitive plates for electrophotography, particularly the type of photosensitive plate comprising three layers and utilizing the persistent internal polarization, based on the above-mentioned viewpoint, by

1. Giving a potential barrier to the surface of the powder granules of the photosensitive layer, a characteristic by which the said barrier is rendered susceptible to incident light;
2. Improving the trap level on the surface of the powder granules, and
3. Increasing the quantum efficiency of the powder granules.

In order to attain the above-mentioned objects, at least one layer of *p-n* junction is employed in this invention as photoconductive fine particles. Actually, there may be a plate having a *n*-type center and a *p*-type external layer, or one having an additional *n*-type layer on

it, or one having a *p*-type center and a *n*-type external layer, or one having an additional *p*-type layer on it.

And moreover, at the boundary of *p*-type and *n*-type layers, it is considered that an *i*-type layer of semi-insulating nature is present, which is an intermediate type of *n* and *p*-types, however, herein we positively introduce and utilize an *i*-type layer to provide a *p-i-n* plate.

With a center of *n*-type as in FIG. 2, the external *p*-type semiconductor is a barrier to electrons so as to increase the dark resistance of the photosensitive layer and to retain surface potential, and the acceptor compensating the free electrons at the *i*-layer plays the role of trapping positive holes produced by the incident light rays. Since the *i*-layer is in close contact with the barrier of the *p*-layer, the positive charge of the trapped positive holes will substantially lower the barrier so that the barrier of the *p*-layer, the positive charge of the trapped positive holes will substantially lower the barrier so that the barrier of the *p*-layer is varied very sensitively and photoconductivity becomes very sensitive.

The present invention will be described more in detail with reference to the embodiment shown in the attached drawing, in which:

FIG. 1 is a cross sectional view of a photosensitive member having a photoconductive layer formed by dispersing a photoconductive powder of the present invention into a binder;

FIG. 2 is a cross sectional view of one example of a photoconductive powder of the present invention; and

FIG. 3 is a characteristic curve of the photosensitive plate as shown in FIG. 1.

FIG. 1 shows a photosensitive plate comprising highly insulating transparent film (polyester, fluorine resin, etc. having a resistivity of $10^{15} \Omega\text{-cm}$) 1, an electrically conductive or insulating base 2, and a photoconductive layer 3 formed between the above-mentioned film 1 and the base 2 by binding the above-mentioned photoconductive fine particles with a binder 4 such as epoxy resin or vinyl acetate.

With this construction, it is possible to obtain a photosensitive plate 1.5 to 10 times more sensitive than the conventional three-layered photosensitive plate, that is, having such sensitivity that an amount of light only one-tenth of several Lux.sec is sufficient to obtain a contrast of 1000 V.

The reason why such a highly sensitive photosensitive plate can be obtained is not fully understood yet. Particularly, it is almost impossible to discuss physically and quantitatively the resin dispersion of the fine particles concerned in this invention.

The only probable explanation is that it is possible to reduce the bulk resistance drastically by having a *p-n* junction form a barrier eliminatable by light, that is, the sensitivity is increased without reducing the contrast because the donor or acceptor density can be sufficiently increased.

In such a construction, a junction similar to a *p-n-p* or *n-p-n* junction is formed towards the direction in which an electrical field is applied and an effect similar to a *p-n-p* or *n-p-n* diode is produced. Electrical charge flows rapidly when the photosensitive plate is exposed to light under a certain critical voltage and the electrical charge persists even when a voltage drop has occurred.

We succeeded in making powder photoconductive substances for *p-n* junctions or *n-p* junctions having the

above-mentioned characteristics by using, for example, a method as described below.

To the surface of powder granules of cadmium sulfide or cadmium selenide, pure or containing impurities, either silver Ag or copper Cu is precipitated and adhered by reduction reaction and these metals are diffused in the interior of the surface or, by substituted reaction, the cadmium Cd is substituted for by silver Ag or copper Cu.

Furthermore, for positively introducing an *i*-layer, when the center is *n*-type, the particles thereof are sintered in a suitable circumference to form Cd vacancies on the surface of the particles or suitably surface treated to add Cu or Ag as an acceptor on the surface, and, by compensating free electrons from donors on the surface, a semi-insulating *i*-layer is formed externally of *n*-type layer. When the center is *p*-type, the particles thereof are sintered in a suitable circumference to make the same Cd rich or surface treated suitably so as to add halogen, indium, gallium etc. on the surface to form an *i*-layer.

The present invention is further illustrated by the following non-limiting examples.

EXAMPLE 1.

In a method for obtaining photoconductive powder having a *p*-type surface layer by making silver adhere to the surface of *n*-type CdS powder granules by reduction,

(1)	Pure CdS available on the market	10 g
	Cadmium chloride	1 g
	Ammonium chloride	0.1 g
	Cupric chloride	0.003 g
	Pure water	4 cc

were mixed and kneaded completely in a beaker.

- After drying completely at 100°C, the dried block was broken into pieces the size of beans, placed in a quartz tube, and sintered for 30 minutes at 600°C in nitrogen ambient atmosphere.
- The sintered product was completely washed with pure water by repeated tilt washing, dried, and then passed through a sieve of 325 mesh to obtain a bright yellow powder.
- The product underwent the so-called silver mirror reaction. The reacting solutions A and B were prepared as follows:

Solution A

1 g of silver nitrate was dissolved in water. Ammonia water was added to this solution carefully until the silver oxide precipitate produced first was almost dissolved again by the excess by ammonia. The solution was filtered and the filtrate was made using up to 100 cc of water.

Solution B

0.2 g of silver nitrate was dissolved in a small amount of water. 100 cc of boiling water was added to the solution followed by the addition of 0.166g of Rochell salt. The solution was boiled for some time. The grey turbid liquid thus obtained was filtered while hot, and the filtrate was used as the solution B.

0.3 cc each of the solutions A and B were diluted with 10 cc of water separately and both diluted solutions were mixed simultaneously with the bright yellow powder obtained in (3). The mixture of these three materi-

als was agitated for about 60 minutes. Then the mixture was washed completely with water by tilt washing and dried. Granules that had precipitated silver adhered to their surface were obtained.

- The dried powder obtained in (4) was placed in a quartz tube and sintered for 60 minutes at 600°C in nitrogen ambient atmosphere. The silver adhered to the surface was heat diffused in the interior of the granules, a *p*-type layer was formed on the surface of *n*-type CdS powder, and activated powder photoconductive substance was obtained.

EXAMPLE 2

In a method for preparing photoconductive powder having a *p*-type surface layer by making copper adhere to the surface of *n*-type CdS powder by reduction,

- 10g of recrystallized pure cadmium chloride and 4 cc of 35 percent hydrochloric acid were mixed with and completely dissolved in 200 cc. Pure hydrogen sulfide was blown into this solution sufficiently to form cadmium sulfide precipitate.
- The precipitate was washed completely with pure water by tilt washing and then completely dried in a vacuum desiccator at 60°C. After drying, the precipitate was crushed by a ball mill for about 5 hours.
- 0.1 g of sulfur was added to the powder obtained in (2). The mixture was placed in a quartz tube and sintered for about 20 minutes at 500°C in nitrogen ambient atmosphere followed by 10 minutes of sintering while exhausting the sulfur vapor.
- The powder obtained in (3) underwent Fehling's reaction. 2 mg of copper sulfate, 20 mg of sodium hydroxide, and 15 mg of reducing agent formaldehyde were dissolved in 10 cc of pure water, respectively and separately. These solutions and the powder were mixed simultaneously and the mixture was agitated for about 30 minutes. The precipitate was then washed completely with water by tilt washing and dried. Granules having a surface with precipitated and adhering copper were obtained.
- The powder obtained in (4) was placed in a quartz tube and sintered for 60 minutes at 600°C in nitrogen ambient atmosphere. Then activated powder photoconductive substance was obtained.

EXAMPLE 3

In a method for preparing photoconductive powder having a *p*-type surface layer by substituting Cd of the surface of powder granule of *n*-type CdS with copper by means of substitution reaction, to the powder obtained by the steps (1) through (3) of the Example 1 was added a solution prepared by dissolving 0.1 cc of sulfuric acid of 96 percent or more concentration and 0.002 g of copper sulfate in 200 cc of pure water. The mixture was subjected to agitation for about 10 hours in a closed-type rotary agitator, washed completely with pure water by tilt washing and dried at about 100°C. The dried powder was placed in a quartz tube and sintered for 60 minutes at 600°C in nitrogen ambient atmosphere. Activated photoconductive powder was obtained.

EXAMPLE 4

In a method for preparing photoconductive powder having a *p*-type layer on the surface by substituting the Cd on the surface of *n*-type CdS powder granule with

silver by means of substitution reaction to the powder obtained by the steps (1) through (3) of the Example 2, was added a solution prepared by adding 0.003 g of silver nitrate and 0.1 cc of concentrated nitric acid to 20 cc of pure water. The mixture was agitated for about 10 hours in a closed-type rotary agitator, washed completely by tilt washing, and then dried at about 100°C. The dried precipitate was sintered for 1 hour at 600°C in nitrogen ambient atmosphere to obtain activated photoconductive powder granules.

EXAMPLE 5

ZnO for electrophotography available on the market was treated in 40-atmospheric-pressure hydrogen at 700°C to increase the electrical conductivity. The ZnO granules were dropped in vacuum continuously from a container maintained at about 25°C and evaporated with Se. This evaporation was repeated several times. Then the granules were dispersed into acrylic resin, and the suspension was applied to a metal plate to a thickness of about 50 μ . The metal plate was then charged by negative corona discharge and an optical image was projected on the metal plate. An electrostatic pattern having a contrast of 300 V was obtained.

EXAMPLE 6

In a method for preparing *n-p-n* type photoconductive substance powder of CdS or CdSe, powder having a *p*-type surface layer obtained by the methods described in the Examples 1 through 4 was mixed with pure water. The mixture received filtration. A small amount of the aqueous solution of a fusing agent (for example, a 0.1 mol aqueous solution of cadmium chloride and 1.0 mol aqueous solution of ammonium chloride) was poured on the precipitate to moisten it, and the excessive solution was suction-filtered. The powder was dried, and then sintered for 60 minutes at 600°C in nitrogen ambient atmosphere, and *n-p-n*-type photoconductive powder was obtained.

EXAMPLE 7

In a method for preparing *p-n*-type photoconductive powder of CdS,

1. to a quantity of *n*-type pure CdS powder was added several percent in weight of copper sulfide. The mixture was ground completely in a ball mill, and then sintered for 2 hours at a temperature within the range of about 700° to 900°C in nitrogen ambient atmosphere to obtain *p*-type powder.

2. The sintered product was first broken into pieces in a mortar and then ground for 24 hours in a ball mill, screened into classes, both the coarse powder and extremely fine powder were removed, and granules within the range of 1 to 20 μ were obtained. These granules were sintered for 30 minutes in a vacuum at 600° to 800°C. An *n*-type layer was formed on the surface of *p*-type granules having sulfur vacancies.

3. The powder was mixed with pure water and filtered, and moistened with a small amount of aqueous solution containing only a halide fusing agent or salts of indium, potassium, etc., again filtered and dried completely, and sintered for about 2 hours at a temperature higher than its melting point in inactive ambient atmosphere. Then a more firm *n*-type layer was formed.

EXAMPLE 8

In a method for preparing *p-n-p*-type photoconductive powder, copper or silver precipitate was adhered to the surface of the *p-n*-type powder obtained in the Example 7 by means of the method described in the Example 1 through 4 and by subjecting the powder to heat diffusion or substitution with Cd.

EXAMPLE 9

In a method for preparing *n-i-p*-type photoconductive powder, Examples 1 and 2 are practiced, except that the amounts of silver and copper are reduced to about less than one-tenth, and the powder is obtained. To 10 g of the obtained powder is added a solution of 30 mg Cu CN, 45 mg of Na CN dissolved in 20 cc pure water to obtain a mixture, which is agitated in a bath of 70°C about 20 minutes. After tilt filtering, it is dried to obtain a Cu₂S layer of *p*-type semiconductivity on the surface of the particles.

EXAMPLE 10

In a method for preparing *n-i-p*-type photoconductive powder, instead of the solution including Cu CN and NaCN in Example 9, a solution of 30 mg AgNO₃ and 0.1 cc concentrated nitric acid is used, by which a *p*-type layer of Ag₂S is formed on the surface of the particles to obtain *n-i-p* type powder.

The method for preparing three layered photosensitive plates of this invention by using the photoconductive powder described in Examples 1 through 10 is as follows:

1. To 10g of photoconductive substance powder of this invention having a *p*-type layer as mentioned above is added 1.5 g of Epicoat 815 (trade name), an epoxy resin with which about 12 percent in weight of an amine family hardener K 61B is mixed, and mixed well.

2. This mixture was transferred on to a smooth aluminum leaf installed on a plane plate and leveled rapidly to a thickness of about 80 microns. To level the mixture, a Mylar insulation film about 25 microns in thickness was placed on the above-mentioned mixture, using a thin metal sheet frame as the spacer. Then using a metal rod having a wedge-like cross section, the mixture was squeezed through the Mylar insulation film, by utilizing the edge of the wedge.

3. Then the entire body was placed in the thermostatic oven, left here for 3 hours at 70°C, to harden the resin. Next, the sensitivity of the three layered photosensitive plate of this invention mentioned above was compared with that of a photosensitive plate of the same composition but prepared by using photoconductive cadmium sulfide of the conventional method and by employing the same method as mentioned above.

The photosensitive plate is positively charged to a surface potential of +1,500V by corona discharge in an illuminated or dark place according to the electrophotographic process mentioned previously. Then, while projecting an optical image onto the photosensitive plate to form an electrostatic latent image, a corona discharge of about the same magnitude and opposite in polarity is applied to the plate to charge it negatively. or an AC corona is applied to remove the electric charge, and then the entire photosensitive plate is exposed to light.

Using this method, the sensitivity of the photosensitive plate was judged on the minimum amount of expo-

sure required to obtain a latent image having sufficiently good contrast. The result obtained was 1 Lux.-sec for the electrophotographic plate of this invention, while the result for the conventional plate was found to be 5 times as large, i.e. 5 Lux.sec. Therefore, this invention is very advantageous in improving speed in an electrophotographic copying machine, in compactizing the machine size due to simplification of the light source, and in cost reduction.

FIG. 3 shows the results of the measurement of the thermal excitation current of the photoconductive substance powder of this invention (the one shown in Example 8) and conventional powder (made by adding 0.003g of cupric oxide to 10g of CdS by sintering, using a fusing agent, and by treating the sintered product in sulfur vapor).

The above-mentioned two kinds of photoconductive powder were mixed in weight ratio of 100 : 14 and the mixture was bound by epoxy resin containing an adequate amount of hardening agent. This mixture was transferred onto the metal electrodes, evaporated onto a sheet of glass at an interval of 0.5 mm and a width of 5 mm, dried for 3 hours at 70°C, and then hardened to form a photosensitive layer.

The photosensitive layer first received sufficient light irradiation from the glass plate side through the inter-electrode gaps. The light was then interrupted and the specimen was kept in the dark. A voltage of 100V was applied across the electrodes and the temperature was decreased gradually from the nitrogen temperature at a constant rate, and the current that flowed through the specimen was measured at each temperature. The peak of the curve shows the trap level of the photoconductive substance. As clearly shown in the curve *a*, the photoconductive substance of this invention has a newly formed trap level compared with the conventional one (curve *b*). This is considered one of the causes of the excellent effect the photoconductive substance displayed when used as an electrophotographic photosensitive plate.

This invention utilizes the *p-n* reversal phenomenon of granule surfaces, which occurs as a matter of course in manufacturing electrophotographic photoconductive substances in accordance with the invention.

The idea of this invention contains various kinds of variations and is also applicable to plates that have no insulating layer on the surface.

For example, when the above-mentioned photosensitive plate was stripped of the insulating layer and charged and exposed, about 10–20 Lux.sec. was found sufficient to obtain a contrast of 500 V. This value is several tenths of that of the conventional ZnO plate and, although its attenuation was quicker than the conventional ZnO, the attenuation was still sufficient for use of the plate in a continuously operating machine.

This invention is applicable to such materials as semiconductors other than the above-mentioned CdS and CdSe, such as ZnO, CdTe, ZnS, ZnSe, Sn₂O, GeS, Ge, Se, Bi₂S₃, GaAs, and PbS which are known, to the use of components for the *p*-region and *n*-region which differ from each other, and to substances which are within the technical range of this invention.

What is claimed is:

1. A photoconductive powder comprising a photoconductive core and a first photoconductive coating, said core exhibiting *n*-type semiconductivity, said first

coating covering said core and exhibiting *p*-type semiconductivity.

2. A photosensitive member comprising the photoconductive powder claimed in claim 1 and a binder therefor.

3. The photosensitive member claimed in claim 2 in which the photosensitive member is a photoconductive layer and including further an overlying insulative layer.

4. Inorganic photoconductive powder comprising a photoconductive core, a first photoconductive coating covering the core and a second photoconductive coating covering the first coating, the core and the second coating each exhibiting the same type of conductivity selected from the group consisting of *n*-type semiconductivity and *p*-type semiconductivity and the first coating exhibiting a type of conductivity different from that of the core and the second coating and selected from the group consisting of *n*-type semiconductivity and *p*-type semiconductivity.

5. The photoconductive powder claimed in claim 4, in which the core and the second coating exhibit *n*-type semiconductivity and the first coating exhibits *p*-type semiconductivity.

6. The photoconductive powder claimed in claim 4, in which the core and the second coating exhibit *p*-type semiconductivity and the first coating exhibits *n*-type semiconductivity.

7. A photosensitive member comprising the photoconductive powder claimed in claim 5 and a binder therefor.

8. A photosensitive member comprising the photoconductive powder claimed in claim 6 and a binder therefor.

9. The photosensitive member claimed in claim 7 in which the photosensitive member is a photoconductive layer and including further an overlying insulative layer.

10. The photosensitive member claimed in claim 8 in which the photosensitive member is a photoconductive layer and including further an overlying insulative layer.

11. Inorganic photoconductive powder comprising a photoconductive core, a first photoconductive coating covering the core and a second photoconductive coating covering the first coating, the first coating exhibiting positively introduced *i*-type semi-insulation and the core and the second coating each exhibiting a different type of conductivity selected from the group consisting of *n*-type semiconductivity and *p*-type semiconductivity.

12. The photoconductive powder claimed in claim 11, in which the core exhibits *n*-type semiconductivity and the second coating exhibits *p*-type semiconductivity.

13. The photoconductive powder claimed in claim 11, in which the core exhibits *p*-type semiconductivity and the second coating exhibits *n*-type semiconductivity.

14. The photoconductive powder claimed in claim 12, in which the core comprises CdS and the second coating comprises a material selected from the group consisting of Cu₂S, Ag₂S, Cu₂O and Ag₂O.

15. The photoconductive powder claimed in claim 12, in which the core comprises CdSe, and the second coating comprises a material selected from the group consisting of Cu₂Se, Ag₂Se, Cu₂O and Ag₂O.

16. The photoconductive powder claimed in claim 12, in which the core comprises CdS, the first coating comprises CdS and the second coating comprises Cu₂S, the second coating being formed on the first coating by chemical substitution reaction.

17. The photoconductive powder claimed in claim 12, in which the core comprises CdSe, the first coating comprises CdSe and the second coating comprises Cu₂Se, the second coating being formed on the first coating by chemical substitution reaction.

18. The photoconductive powder claimed in claim 12, in which the core comprises CdS and the first coating comprises n-type CdS which is rendered i-type semi-insulative by the addition of Cu acceptor impurity thereto.

19. The photoconductive powder claimed in claim 12, in which the core comprises CdS and the first coating comprises n-type CdS which is rendered i-type semi-insulative by the addition of Ag acceptor impurity thereto.

20. The photoconductive powder claimed in claim 12, in which the core comprises CdSe and the first coating comprises n-type CdSe which is rendered i-type

semi-insulative by the addition of Cu acceptor impurity thereto.

21. The photoconductive powder claimed in claim 12, in which the core comprises CdSe and the first coating comprises n-type CdSe which is rendered i-type semi-insulative by the addition of Ag acceptor impurity thereto.

22. The photoconductive powder claimed in claim 12, in which the second coating comprises Cu₂O formed on the first coating by Fehling reaction.

23. The photoconductive powder claimed in claim 12, in which the second coating comprises Ag₂O formed on the first coating by the chemical reaction of a soluble silver salt and an alkaline material.

24. A photosensitive member comprising the photoconductive powder claimed in claim 11 and a binder therefor.

25. The photosensitive member claimed in claim 24 in which the photosensitive member is a photoconductive layer and including further an overlying insulative layer.

* * * * *

25

30

35

40

45

50

55

60

65