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PROCESS FOR THE PRODUCTION OF A LIGHT SENSITIVE BODY HAVING AN INSULATING PHOTOCONDUCTIVE LAYER

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ABSTRACT OF THE DISCLOSURE

Process for producing a light sensitive body having an insulating photo-conductive layer which comprises dispersing a photo-conductive cadium sulfide powder having an average grain size of less than 1.5 microns in an electrically insulating thermo-setting resin having a specific resistance (by volume) of at least $10^{11}\Omega$ cm. at room temperature. The dispersion is applied to a support and heated to thus harden or cure the resin and to simultaneously heat treat the fine cadmium sulfide powder and the resin.

This invention relates to a process for the production of a light sensitive body and more particularly, to a process for the production of a hard, highly sensitive, insulating photoconductive layer suitable for use in electrophotography.

Some photoconductive inorganic compounds are well known to be useful as an insulating photoconductive layer for electrophotography. For example, there are metals, such as, sulfur and selenium, and metal compounds, such as, oxides, sulfides and selenides of zinc, cadmium, mercury, antimony, bismuth and lead, titanium oxide. These materials are formed in layers on a base plate, in particular, a metal plate or paper. In some cases, insulating photoconductive layers are formed by dispersing these materials in an electrically insulating film forming binder. The most widely known and practically used of these materials are selenium and zinc oxide. The other materials have not been put to practical use yet and no literature has been disclosed with respect thereto. In order to obtain electrophotographic images using these materials, an electrostatic charge is first given to the surface of the coating thereof in a dark chamber, for example, by corona discharge, whereby to impart light sensitivity thereto, and then the insulating photoconductive layer is exposed to light by an ordinary photographic method.

The electrostatic latent image obtained by the exposure to light is developed by applying a fine powder of colored resin having electric charges. The fine powder of colored resin is fixed on the insulating photoconductive layer, as it is or after transfer to a suitable support, by means of heat or solvent. When a transfer is carried out, the residual fine powder on the light sensitive body is removed and the light sensitive body is reused.

Selenium, which is widely known and practically used, is coated on a metal plate, in particular, an aluminum plate to form a layer of glassy selenium. This is used as a light sensitive body to be used repeatedly. The sensitivity thereof is highest, corresponding to ASA 2–10. The glassy selenium is suitable for repeated uses, since its hardness is high and its surface is mirror-like. On the other hand, zinc oxide, the other material which is widely known and practically used, is dispersed in an electrically insulating resin binder and applied to a paper, followed by drying, whereby an electrophotographic sensitive body, called light sensitive paper, is formed. This light sensitive paper has a

sensitivity of ASA 0.01–0.2. Images are directly formed and fixed on the paper. Because of this the color is substantially white. This zinc oxide dispersed layer may be applied to a metal base, but the resulting light sensitive body is unfavorably compared with that of selenium, the hardness of the coating and the sensitivity being lower, and therefore, it is unfit for repeated uses. Moreover, the characteristics, in addition to the lower hardness and sensitivity, deteriorate once it is exposed to light. Other than selenium and zinc oxide, only titanium oxide has been noted lately for its practical use, and the others are only described in the literature. The selenium light sensitive body which can be used repeatedly exhibits excellent characteristics of light sensitivity, hardness of the light sensitive layer and effect of pre-exposure to light, but is accompanied by the following disadvantages. That is to say, the production of the material is very difficult. The selenium used as an insulating photoconductive layer for electrophotography is glassy and is formed into a uniform film on an aluminum plate by the vapor deposition in vacuum. The plant for its production should be of a large scale and provided with means for vacuum vapor deposition. The efficiency of such production is low. Another disadvantage lies in that the control of additives to be added for the purpose of enhancing the sensitivity and improving other characteristics is very difficult due to the vapor deposition in vacuum. Furthermore, the glassy selenium is of one solid phase of selenium in a supercooled state. This tends to be crystallized by the influences of temperature, moisture in the air and other materials, so the deterioration of its characteristics is promoted at high temperature and humidity, resulting in shortening of its useful life. In the case of zinc oxide, coloring matters are added for the sensitization, but this causes such defects that the length of life is much shorter than the selenium light sensitive body, since these coloring matters are thermally weak and a relatively rapid deterioration of the characteristics is brought about by corona discharge and repeated exposure to light.

In order to overcome the foregoing disadvantages, that is, difficulties in production, low resistance to heat and contamination in the selenium light sensitive body, low sensitivity, low hardness of the light sensitive layer, the effect of pre-exposure to light and instability to thermal shock in the zinc oxide light sensitive body, the present invention provides a highly insulating photoconductive layer, in particular, electrophotographic light sensitive body, which can be readily produced, has a light sensitivity which is the same as or more than that of the selenium light sensitive body, is very stable thermally, is substantially free from the effect of pre-exposure to light, is sufficiently resistant to repeated uses and has excellent hardness in the light sensitive layer.

The electrophotographic light sensitive body of this invention has been developed with the objects described above and a process for the production thereof consists in dispersing a fine powder of photoconductive cadmium sulfide, having an average grain size of less than 1.5 micron, in a solvent solution of thermosetting resin having a specific resistance by volume of at least $10^{11}\Omega$ cm., applying the resulting dispersion to a suitable support, such as metal, and heating the support, thus coated, whereby to promote the hardening of the resin and to effect the heat treatment of the cadmium sulfide powder and resin.

The insulating photoconductive layer means a layer of such material that does not or scarcely exhibits electric conductivity in a dark place, but exhibits or increases it upon exposure to light or other radiations. A method for the discrimination of the insulating photoconductive layer of this invention is, for example, to impart electrostatic charges to a free surface side of the insulating

photoconductive layer formed on an electrically conductive support in a dark place by means of corona discharge. In this case, the electrostatic charges imparted can be maintained for a considerably long time in a dark place. The polarity of the charge exhibits a difference in the rectifying property and light sensitivity and differs by a material used. A selenium-type light sensitive body is generally positively charged (plus) and a zinc oxide-type light sensitive body is generally negatively charged (minus). The longer the time for maintaining electrostatic charges in a dark place, the greater is the electrically insulating property. This is preferable. In general, a time required for electric charges on a surface to decrease half of its initial value is several tens to thousands minutes. When a suitable light or radiant ray is radiated upon an insulating photoconductive layer having electric charges on the surface, the electric conductivity is increased and the surface charges are rapidly discharged. The attenuation velocity of surface charges during the radiation of light is as follows: It is 0.1–0.2 second for selenium-type light sensitive bodies and 2–20 seconds for zinc oxide-type light sensitive bodies, though being different by the degree of dye sensitization, as represented by a time required for the surface charges to decrease half of its initial value in radiating by the use of a tungsten filament lamp of 100 lux. When light is radiated upon a surface of light sensitive body prior to charging it, in some cases, the keeping capacity of electrostatic charges in a dark place is lowered and the attenuation of charges in radiating light is accelerated or retarded. This is called the effect of pre-exposure to light in general, which must be avoided if it is desired to obtain stable images constantly.

An object of the present invention is to provide a light sensitive body which has the same capacity for keeping an electrostatic charge in a dark place and the same attenuation velocity of surface charges in radiating light as a selenium light sensitive body.

Another object of this invention is to provide an electrophotographic light sensitive body capable of being used repeatedly to give stable images substantially free from the effect of pre-exposure to light.

A still further object of our invention is to provide an electrophotographic light sensitive body which is very stable thermally, has a high strength of the coating and long life and can be used continuously repeatedly.

A still further object of our invention is to provide an electrophotographic light sensitive body which can be produced in a very simple manner with low cost and on a large scale.

A still further object of our invention is to provide an insulating photoconductive layer, the electric resistance of which is very high or hardly represents electric conductivity in a dark place, but the electric resistance of which decreases or represents electric conductivity during the exposure to light or other radiant energy.

The insulating photoconductive layer of the electrophotographic light sensitive body in accordance with the invention can be adapted, therefore, not only for electrophotography, but for means for converting signals of light or other radiant energy into electric signals, for example, in a photocell, image intensifier and image converter.

As cadmium sulfide is a most excellent photoconductive material as is well known, but has a low electric resistance in a dark place in general, that is, 10^3–$10^8\Omega$ cm., this being much less than the 10^{13}–$10^{15}\Omega$ cm. required for an insulating photoconductive material in electrophotography, it has not been put to practical use yet in spite of its possibilities. The studies on cadmium sulfide have been mainly concentrated in sintered bodies, in the production of large single crystals and in the production of sintered bodies from which the unevenness of electric properties among gains is eliminated as far as possible. This results in practical use in photocells wherein the characteristics of cadmium sulfide are adequately utilized.

On the contrary, our efforts have been directed to reduction of the sizes of crystals or primary grains, that is, to enlargement of surface areas thereof, and thereby to introduction of the unevenness of electric properties at the contacts among grains or the electric barriers, whereby the electric resistance in a dark place is increased. Although it remains unknown whether such reasoning is correct or not, an electrophotographic light sensitive body which can be favorably put to practical use is obtained by dispersing a fine powder of photoconductive cadmium sulfide having an average grain size of less than 1.5 micron in a synthetic resin binder, applying the dispersion to a support and drying to give an insulating photoconductive layer of resin-finely divided photoconductive material dispersion. In this case, of course, the proportions of the binder and fine powder of cadmium sulfide should be strictly selected, since the electric conductivity of the insulating photoconductive layer is controlled by the contacts among grains. It is found that suitable proportions of the binder and cadmium sulfide is within 80–40% by volume of the binder to 20–60% volume of cadmium sulfide, preferably within 68–58% by volume of the former to 32–42% by volume of the latter. This varies with the binder. As the binder to be used, a synthetic resin having a specific resistance by volume of more than $10^{11}\Omega$ cm., is preferably selected so as to maintain the electric resistance of the insulating photoconductive layer desired.

EXAMPLE 1

A dispersed solution having the following composition was prepared:

	Parts by wt.
Copolymer of n-butyl methacrylate and i-butyl methacrylate	18.2
Fine powder of photoconductive cadmium sulfide	40.0
Toluene	56.3
Total	114.5

This dispersed solution was applied to a paper and dried under the following conditions: Drying temperature—50° C.; drying time—20 hours; coating thickness—about 30 microns.

Good results were obtained when this light sensitive paper was negatively charged (minus). The charging by corona discharge at −7.0 kv. gave a surface potential of 600–650 v. The attenuation velocity of the surface potential in a dark place was 8–10 minutes as represented by the time required for the surface potential to decrease half of its value and in radiating light of 20 lux by the use of tungsten-filament lamp, 1.5 seconds are represented by the same. Images were obtained by such an exposure to light as in chlorobromide printing paper for silver salt photography.

In the Example 1, an electrophotographic light sensitive paper was shown, but the light sensitive paper could be reused by transferring the resulting images to another paper, followed by cleaning. In addition to the synthetic resin shown in Example 1, cellulose type resins, polyesters, phenol resins, epoxy resins, amino resins, polyurethane resins, silicone resins and copolymer of vinyl acetate vinyl chloride may be used.

The electrophotographic light sensitive paper of the Example 1 has a low coating hardness and is not suitable for repeated uses, for the support is of paper.

It is required for repeated uses that a metal sheet, metal pipe or other elastic or flexible materials be used as a support and that the mechanical strengths of the insulating photoconductive layer, for example, the resistance to abrasion and furthermore, the resistance to chemicals and weathering, be excellent. To this end, the use of a binding agent of thermosetting type resin is recommended. Illustrative of the thermosetting resins are phenol resins, xylene resins, urea resins, alkyd resins, unsaturated poly-

ester resins, furan resins, silicone resins, epoxy resins and acrylic resins.

The invention is further illustrated by the following examples:

EXAMPLE 2

An electrophotographic light sensitive body was prepared by mixing a thermosetting acrylic resin, as a thermosetting resin, and cadmium sulfide, as a photoconductive material, to give a composition as shown in Table 1, the average grain size of the cadmium sulfide being 0.2 micron, applying the resulting dispersion to an aluminum sheet and subjecting it to a heat treatment at 150° C. for 30 minutes. In Table 1 are shown the surface potentials after 2 seconds from the charge by corona discharge in a dark place and the time required for the surface potential to decrease by half when light of 8 lux was radiated upon the electrophotographic light sensitive body charged by a tungsten-filament lamp. The thickness of the coating was approximately 30 microns after drying.

It is evident from the data of Table 1 that the allowable range in the proportions of a binder and cadmium sulfide powder is less than that of the zinc oxide type sensitive bodies in the prior art. The most excellent dispersions is D–35 corresponding to the composition ratio by volume of 35.5 cadmium sulfide to 64.5 binder. D32–37 show characteristics suitable for use as insulating photoconductive bodies for electrophotography. These light sensitive bodies are very excellent in lustre, hardness, adherence between the insulating photoconductive body and aluminum sheet and resistance to wearing, and can be used repeatedly.

TABLE 1.—COMPOSITION AND CHARACTERISTICS OF MATERIALS OF EXAMPLE 2

Dispersion No.	CdS powder (g.) [1]	Magicron [2] 200 clear (g.)	Surface potential volt	Time for half-value, sec.
D-31	150	35	60	1.1
D-28	150	45	70	
D-27	150	55	67	
D-26	150	65	55	
D-25	150	75	56	
D-29	150	85	58	
D-32	150	95	102	0.8
D-33	150	105	190	4.5
D-34	150	115	1108	30
D-35	150	125	625	4.8
D-36	150	135	1085	30
D-37	150	145	1080	30

[1] Cadmium sulfide powder: photoconductive powder, average grain size 0.2 micron.
[2] Thermosetting acryl resin lacquer (Kansai Paint Co., Ltd.).

EXAMPLE 3

A cylindrical light sensitive body was prepared by applying the dispersion of D–35 of the Example 2 to an aluminum pipe by spraying and subjecting it to a heat treatment at 150° C. for 30 minutes. The light sensitive body presented a lustrous surface like enamel. The thickness of the coating was approximately 35 micron after hardening.

EXAMPLE 4

A dispersed solution having the following composition was applied to an aluminum foil and subjected to a heat treatment at 150° C. for 60 minutes to produce a light sensitive body.

	Parts by wt.
Million No. 1 M clear [1]	65
Photoconductive cadmium sulfide (used in Example 2)	75
Million No. 1 M thinner	120
Total	260

[1] Epoxy resin type paint vehicle produced by Kansai Paint Co., Ltd.

EXAMPLE 5

A dispersed solution having the following composition was applied to an aluminum plate and subjected to heat treatment at 150° C. for 75 minutes to produce a light sensitive body.

	Parts by wt.
Silicone varnish KR 206 [1]	48
Photoconductive cadmium sulfide (used in Example 2)	100
Xylene	200
Total	348

[1] Produced by Shin-Etsu Chemical Industry Co., Ltd.

EXAMPLE 6

A dispersed solution having the following composition was applied to an iron pipe and subjected to heat treatment at 150° C. for 30 minutes to produce a light sensitive body.

	Parts by wt.
Photoconductive cadmium sulfide powder (used in Example 2)	100
Amyllac No. 2 clear [1]	42
Amyllac No. 2 thinner	200
Total	342

[1] Butylated melamine resin, a paint vehicle for high temperature baking consisting of non-drying, short oil alkyd resin and epoxy resin, produced by Kansai Paint Co., Ltd.

In the foregoing examples, cadmium sulfide powder is buried in the free surface of the insulating photoconductive layer and because of this, the strength of the coating is lower, as compared with a coating having no cadmium sulfide powder or a small content thereof. In order to eliminate such defect, a layer having no or small content of cadmium sulfide powder may be applied to the surface layer to be 0.5–1 micron in thickness.

What is claimed is:

1. A process for the production of a light sensitive body having an insulating photoconductive layer, which comprises dispersing a fine powder consisting of photoconductive cadmium sulfide having an average grain size of less than 1.5 microns in an electrically insulating, acrylic thermo-setting resin having a specific resistance by volume of at least $10^{11}\Omega$ cm. at room temperature, applying the resulting dispersion to a support, and heating the support thus coated to a temperature of at least 150° C. for at least 30 minutes to harden the resin and simultaneously to carry out heat treatment of the fine powder of cadmium sulfide and resin.

2. The process according to claim **1** wherein the proportion of said photoconductive cadmium sulfide in said layer is from 20% to 60% by volume.

3. The process according to claim **1** wherein the proportion of said photoconductive cadmium sulfide in said layer is from 32% to 42% by volume.

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