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PHOTOCONDUCTIVE INSULATING MATERIALS

Katsuo Makino and Iwao Sawato, Odawara-shi, Kanagawa, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Ashigara-Kamigun, Kanagawa, Japan

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ABSTRACT OF THE DISCLOSURE

Disclosed is a photoconductive insulating composition comprising an organic resin binder or low melting glass having dispersed therein particles of cadmium sulfide or mixtures of cadmium sulfide and cadmium carbonate having iodine absorbed thereon.

The present invention relates to photoconductive insulating materials and in particular to photoconductive insulating materials of high photographic speed for use in electrophotography, which comprises a powdery mass of finely divided, photoconductive materials dispersed in a binding agent therefor. More specifically, the invention relates to photoconductive insulating materials prepared by adding iodine to a powdery mass of finely divided, photoconductive materials composed mainly of cadmium sulfide or both cadmium sulfide and cadmium carbonate such, for example, as a podwer mass of the composition: $(CdS)\cdot nCdCO_3$ (n=0—4), and dispersing the resulting mixture in a binding agent therefor.

The words "photoconductive insulating materials" should be understood to mean materials which exhibit a specific resistivity of at least 10^8 ohms-cm. in a dark place or in a place where any sort of radiations are not present, and the electric resistance of which is lowered upon exposure to light or radiation.

Said photoconductive insulating materials, therefor, may be suitably used as a photosensitive material for various kinds of electrophoto converting machinery and means, as well as a photosensitive material for all sorts of electrophotographic processes. Said photoconductive insulating materials have been employed as an electrophoto converting material, for example, in the field of optical image transducing machinery and also as photoelectric cells, image intensifiers, vidicon and phototape and apparatus for converting an X-ray image into a visible ray image.

In the art of electrophotography a number of processes have previously been proposed. A process which has long been known will now be described. In the step of creating an image on an electrophotographic material, a photosensitive member is first made electrophotosensitive by application of an electrostatic charge for example, by corona discharge and the like in a dark place. The electrophotosensitive member thus charged electrostatically is then exposed to light by means of an ordinary photographic process. Upon exposure to light, the electrostatic charge is discharged depending on the intensity of light projected thereto, thereby forming an electrostatic latent image of the configuration corresponding to an original picture to be photographed. The electrostatic latent image may then be rendered visible by deposition of a finely divided, charged, and colored powder material. Then the developed powder image is fixed in place on the surface of the photosensitive member or on the surface of a suitable substrate after being transferred to the substrate. After the completion of the transfer, the surface of the photosensitive member is cleaned of residual colored

powder and the photosensitive member becomes reusable. Said procedures hereinbefore mentioned are most ordiary in electrophotography. Although many modifications may be possible in the process, it may be considered that the nature of a photoconductive insulating material of the photosensitive member remains unchanged in itself.

In case of duplicating, while using an automatic duplicator and the like, it is required that the electro-photosensitive member be of higher photographic speed. It is further required that the electrophotosensitive member which is employed in the apparatus for transferring a developed image have sufficient electrophotographic characteristics and mechanical strength to stand continuous and repeated use. Although we have investigated a plurality of photosensitive materials for an automatic transferring apparatus which are capable of standing the continuous, repeated use, comprising a photoconductive powder composed mainly of cadmium sulfide dispersed in a binding agent therefor, none of them is comparable with a photoconductive material composed mainly of vitreous selenium in point of photographic speed, gamma and light-fatigue (preexposure effect). The term "gamma" will hereinafter be described.

Now, in accordance with the present invention it has been found that improved photographic speed, gamma or light-fatigue can be effected by the addition of iodine. In other words, we have succeeded in preparing photoconductive materials for an automatic transferring apparatus which are being capable of standing continuous and repeated use and which are approximately equal to vitreous selenium photoconductive material. An electrophotosensitive member prepared from the photoconductive insulating materials of this invention can further be used favorably in an apparatus of the type in which an image created on the surface of a photosensitive member is directly fixed thereon.

The words "potential acceptance" means the surface potential exhibited by a photosensitive member for acceptance of an electrostatic charge by means of corona discharge and the like applied to an electrophotosensitive member, and the words "exposure time for half-decay" is the period of time required for the reduction of the surface potential by half upon exposure to light. The higher the potential acceptance, and the shorter the exposure time for half decay, the more the electrophotographic material is preferred. These factors become inferior, in general, if the material is exposed prior to use to light of strong intensity. Especially, the potential acceptance is lowered. This phenomenon is designated as light-fatigue or preexposure effect. Although the existence of a definite relationship is not seen between the potential acceptance and dark resistivity of a photoconductive material, it is generally concluded that the higher is the dark resistivity, the higher the potential acceptance becomes. In addition to this, the electrophotographic photosensitivity of a photoconductive material is considered to be related to the exposure time for half decay.

Cadmium sulfide powder has previously been known as a photoconductive material. We have found that powder comprising a cadmium sulfide and cadmium carbonate is favorable as a photoconductive material for electrophotography. Material of this composition receives electrostatic charges of both positive and negative polarities upon corona discharge and the like. It thereby comes to have approximately equal potential acceptance, and photographic speeds (exactly speaking, it is of slightly higher photographic speed when it is negatively charged). The material, however, is unfavorable in the respect of photographic speed, preexposure effect and gamma, etc., as heretofore mentioned, so that there is necessity for removing these defects.

By incorporating iodine into the material, as follows, characteristics thereof are improved to a certain extent. Iodine is dissolved in ethyl alcohol and added to a powdery mass composed of finely divided cadmium sulfide or both cadmium sulfide and cadmium carbonate. Thereby the dissolved iodine is adsorbed on the surfaces of the fine particles. Ethyl alcohol is thereafter separated from the fine particles, and they are dried to yield a photoconductive powder of high photographic speed. The photoconductive powder is then dispersed in a binding agent composed of organic resins and is finally applied on the surface of a suitable substrate to produce a photosensitive member for electrophotography. It is found from the measurement of physical properties thereof that the photographic speed becomes several times as high as that of photographic material containing no iodine, the light fatigue thereof is lowered and the gamma value increases. The gamma is represented by n in the following formula:

$$Teh \alpha L^{-n}$$

showing the relation between exposure illumination L and exposure time for half-decay Teh. It is not clear why these characteristics were improved. Moreover, said characteristics may be controlled by subjecting the powdery mass to baking after the adsorption of iodine. As the organic resin binder, there may be employed a number of binding agents of the type which dry at normal temperatures, which set by virtue of a catalyst, or which are thermosetting, depending on the object for which the photoconductive material is utilized. In the case of employing a resin of the thermosetting type, the fine powder of photoconductive dispersed material may also be favorably influenced by action of the heat during the course of the heat treatment which is carried out with the intention of causing the resin to set after application. As a binder, an inorganic polymer, such as, a low melting glass may also be utilized. The invention will now be more clearly illustrated by way of examples, as follows:

EXAMPLE 1

Cadmium sulfide of photoconductive property was homogeneously dispersed in pure ethyl alcohol, and was added dropwise to an alcoholic solution of iodine, containing 40 gm. of iodine per 1000 ml. of the solution, in accordance with the prescription in Table 1, while stirring. The iodine was thereby adsorbed in the cadmium sulfide. After allowing the mixture to stand for several hours, the supernatant liquid was removed therefrom, followed by drying under vacuum. Thereafter, the powdery mass, containing adsorbed iodine, was mixed with an amount of binder in accordance with the prescription in Table 1, and treated in a ball mill to effect dispersion, and to yield photoconductive paints. The binder employed in the example was an acrylic clear paint of the thermosetting type, commercially available under the trademark "Magikuron No. 200 Clear" from Kansai Paint Co., Ltd. The photoconductive paint thus prepared was applied onto the surfaces of aluminum sheets to produce coatings of various thicknesses. The coatings were dried and baked at temperatures of 150°, 200° and 250° C., respectively, to produce photosensitive members for electrophotography. The photosensitive members were caused to receive an electrostatic charge under corona discharge at −7.0 kv., and the potential acceptances and the exposure times for half decay thereof were measured. It was seen that the potential acceptance and the exposure time for half decay increased as the thickness of the coating became larger, respectively. It could be shown that the potential acceptance was related to the exposure time for half decay through one curved line, for a group of photoconductive materials which were produced from the same photosensitive paint and under the same baking condition. By utilizing the relation, above described, exposure times of half decay of photosensitive members,

when the potential acceptance is 500 volts, which were produced from various photosensitive paints under the different baking conditions, may be calculated. Exposure times for half decay thus calculated are shown in the term of Teh in the Table 1. Signs, A, B and C represent the following baking conditions: 150° C. for 30 mins.; 200° C., for 60 mins., and 250° C., for 30 mins., respectively. Although some exceptions may be observed, we have confirmed that the photographic speed increases as the amount of iodine added becomes greater.

It has not been confirmed whether all the iodine added is present within a body of the photoconductive material thus produced or not. It may be supposed that a small amount of the iodine is probably evaporated off during the course of the manufacturing procedures therefor. The fact that the photographic speed increases as the baking temperature becomes higher, is considered to show the baking effect of the cadmium sulfide powder containing the adsorbed iodine, as well as the baking effect of the binding agent.

TABLE 1

	Cds, g.	Iodine solution, ml.	Powdery mass of CdS and I, g.	Binder (solid value), g.	Teh, sec. A	B	C
Sample 1---	217	0.00	100	41.7	5.5	2.0	2.2
Sample 2---	217	0.95	100	41.7	7.5	2.2	1.8
Sample 3---	217	9.5	100	41.7	4.3	2.25	1.95
Sample 4---	217	85.0	100	41.7	3.5	1.45	0.92
Sample 5---	217	500.0	100	41.7	2.3	1.8	1.4

EXAMPLE 2

A powdery mass composed of cadmium sulfide and cadmium carbonate, having the composition

$$CdS \cdot 1.5CdCO_3$$

was added, as in the preceding example, with an amount of iodine in accordance with the prescription in Table 2. Thereafter, the powder thus prepared was incorporated with an acrylic resin paint of the thermosetting type, sold under the trademark "Magikuron No. 200 Clear," to yield the desired photosensitive members for electrophotography. Furthermore, exposure times for half decay Teh, when the potential acceptance was 500 volts, were calculated with reference to both the case when the photosensitive member received a positive electrostatic charge, by means of corona discharge at minus 7.0 kv. and in the case when a negative electrostatic charge was applied by means of corona discharge at minus 7.0 kv., the same manner as described in the preceding example. The results therefrom are mentioned in Table 2. It is clearly shown that photographic speed increases by the addition of iodine. The trend is identical whether in the case of a positive electrostatic charge or in the case of a negative charge. The gamma values n are calculated from the relation between the exposure illumination and the exposure time for half decay, as shown in Table 2.

Effects on improving the light-fatigue are also mentioned in Table 2. In general, light-fatigue attains to a great extent when Magikuron No. 200 Clear is used as a binder, so that this example is suitable to illustrate said effects which result from the addition of iodine. The potential acceptance measured after achieving the light-fatigue state is considered to exhibit the degree of light-fatigue. The more the degree of light-fatigue attains an extreme extent, the more the potential acceptance is lowered. In Table 2, there is shown the ratio of potential acceptance in the light-fatigue state to potential acceptance, after being left to stand in a dark place for a long period of time. The former is obtained by measuring the potential acceptance of a photosensitive member after the lapse of 5 mins. from exposure to light of a definite intensity for a constant period of time. It should be understood that the effect of improving the light-fatigue of the member

increases with the amount of iodine added. The light-fatigue phenomenon will, of course, be improved also by varying the kind of binder.

TABLE 2

	$CdS.CdCO_3$ powder, g.	I_2 soln., ml.	$CdS.CdCO_3$ containing I_2, g.	Binder (solid value), g.	Teh		n	Light-fatigue
					−7.0 kv.	+7.0 kv.		
Sample 6	322.5	0.00	155	67.7	4.2	4.4	0.70	0.02
Sample 7	322.5	0.13	155	67.7	2.5	3.6	0.89	0.07
Sample 8	322.5	1.27	155	67.7	2.1	3.1	0.80	0.10
Sample 9	322.5	12.7	155	67.7	1.6	3.1	0.80	0.16
Sample 10	322.5	127	155	67.7	1.6	2.3	0.79	0.03
Sample 11	322.5	1,270	155	67.7	0.8	1.0	0.86	0.40

The base powder employed in Example 2 was of the formula $CdS \cdot 1.5CdCO_3$. However, it is not obvious what kind of crystalline or particle structure the composition comprises. It shows diffraction patterns of both cadmium sulfide and cadmium carbonate, which are independent each other, upon examination using the X-ray diffraction technique. Even if a cadmium sulfide powder and a cadmium carbonate powder are mechanically mixed, however, there is not yielded a powdery mass that exhibits superior characteristics, as seen in the Sample 6 of Example 2. The molar ratio of cadmium carbonate to cadmium sulfide preferably falls within the range up to 4.

Although an ethyl alcohol solution containing only iodine as an additive is employed in the examples hereinbefore illustrated, a small amount of other additives may be used together with the iodine without impairing the effect of iodine.

We claim:

1. A photoconductive insulating composition consisting essentially of an electrically insulating binder having a specific resistivity of at least 10^8 ohm-cm. when not exposed to electromagnetic radiation and selected from the group consisting of organic resin binders and low melting point glass and having dispersed therein a finely divided photoconductive material consisting essentially of cadmium sulfide, cadmium carbonate and iodine, where there is a maximum of about one quarter mol of iodine per mol of cadmium sulfide and where the iodine is adsorbed in particles of cadmium sulfide-cadmium carbonate.

2. A photoconductive insulating composition consisting essentially of an electrically insulating binder having a specific resistivity of at least 10^8 ohm-cm. when not exposed to electromagnetic radiation and selected from the group consisting of organic resin binders and low melting point glass and having dispersed therein a finely divided photoconductive material consisting essentially of cadmium sulfide, cadmium carbonate and iodine, where there is about $1\%_{1000000}$ to about $1\%_{100}$ mol of iodine per mol of cadmium sulfide and where the iodine is adsorbed in particles of cadmium sulfide-cadmium carbonate.

3. The composition of claim **1** wherein the ratio of CdS to $CdCO_3$ in said composition is in the range greater than 0 to approximately 4.

4. The composition of claim **2** wherein the ratio of CdS to $CdCO_3$ in said composition is in the range greater than 0 to approximately 4.

5. The method for producing a photoconductive insulating composition comprising mixing a finely divided photoconductive material selected from the group consisting of cadmium sulfide and cadmium sulfide-cadmium carbonate with an organic solvent solution of iodine, drying to drive off said solvent and leave said iodine adsorbed in said finely divided photoconductive material, and dispersing the finely divided photoconductive material with adsorbed iodine in an electrically insulating binder having a specific resistivity of at least 10^8 ohm-cm. when not exposed to electromagnetic radiation and selected from the group consisting of organic resin binders and low melting point glasses.

6. A photoconductive insulating composition produced in accordance with the method of claim **5.**

7. The method according to claim **5** wherein said organic solvent is an alcohol.

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JOHN DANIEL WELSH, Primary Examiner

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