United States Patent Office

3,743,609
Patented July 3, 1973

3,743,609

PROCESS FOR PRODUCING PHOTOCONDUCTIVE MATERIALS

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No Drawing. Filed Dec. 23, 1971, Ser. No. 211,726
Claims priority, application Japan, Dec. 26, 1970, 45/119,052
Int. Cl. H01c *7/08;* G03g *5/08*
U.S. Cl. 252—501 1 Claim

ABSTRACT OF THE DISCLOSURE

A process for producing a photoconductive powder according to the valence control method, in which a photoconductive inorganic powder is fired in the presence of an activator, a coactivator and a flux, characterized in that the firing is effected in the presence of a dispersant having such property that it contacts with the photoconductive powder, without melting at the firing temperature, and does not fuse nor agglomerate the photoconductive powder. The process is particularly applicable to photoconductive powders containing cadmium sulfide, cadmium selenide or cadmium sulfoselenide.

This invention relates to a process for producing photoconductive fine powders of cadmium sulfide, cadmium selenide, cadmium sulfoselenide, etc.

As is well known, photoconductive powders have been used in the form of resin-bound layers, sintered mass or resin-coated dusts, for a device for changing signals of light or radiation into electric signals which are useful for electrophotography, e.g. image converters, image intensifiers, photocells, etc.

In the case of a cadmium sulfide type photoconductive powder, in general, a pure cadmium sulfide powder is mixed with an acceptor-forming activator such as copper or silver, a donor-forming coactivator such as halide, and a flux such as cadmium chloride, sodium chloride or zinc chloride, and then the resulting mixture is fired at a temperature above the melting point of the flux to carry out the atomic valence control, whereby a photoconductive powder having various characteristics can be obtained. Ordinarily, however, several to several ten cadmium sulfide particles fuse to one another at the time of firing to form a photoconductive powder of about several microns to 30 microns in particle size. The degree of particle size of such photoconductive powder frequently brings about a great problem. For example, in forming a photosensitive layer, the degree of particle size influences the uniformity of the photosensitive layer. That is, if the particle size is large, the surface smoothness of the photosensitive layer is injured. Further, in forming a coating film by use of a dispersion of the powder in a resinous binder, the dispersion should be made high in viscosity in order to lower the sedimentation velocity of the particles, with the result that there are brought about such drawbacks that not only the coating operation is extremely difficult but also bubbles become entrained in the resulting photosensitive layer.

The above-mentioned drawbacks due to large particle size brings about degradation of image quality in the case of image-forming photosensitive members for use in electrophotography, image converters, image intensifiers, etc.

When applied to an electrophotographic photosensitive member, a fine photoconductive powder gives such advantages that the photosensitive member is greatly decreased in fog, increased in contact portions of individual particles, and increased in electric resistance. Further, the uniformity of the photosensitive layer due to incorporation of fine photoconductive powder has such merits that the damage of photoelectric means due to local eddy currents can be prevented and the distance between electrodes can be made small.

For the production of a photoconductive powder, which is finer than that produced in the above-mentioned manner, there may be thought of the following processes:

(1) The prior art photoconductive powder is further pulverized.

(2) In the step of producing the photoconductive powder, the firing is effected by use of no or smaller amount of flux to inhibit the growth of crystals.

(3) In the step of producing the photoconductive powder, the firing is effected at below the melting point of the flux to inhibit the growth of crystals.

According to process (1), however, the resulting crystals are far lower in photosensitivity than the prior art photoconductive crystals. Further, according to processes (2) and (3), sufficient activation cannot be accomplished to make optional valence control impossible, with the result that no high sensitivity material can be obtained.

As a specific process, there has also been known the following process:

(4) A process for producing a high sensitivity fine photoconductive powder having a particle size of less than 5 microns by mixing a cadmium sulfide powder with suitable amounts of an activator, a coactivator and pure water, and treating the resulting mixture at elevated temperature and pressure to recrystallize the cadmium sulfide.

This process, however, is required to be carried out at high temperature and pressure for a long period of time (about 50 hours), and hence is low in practicality.

The present invention is a process for producing a fine photoconductive powder by firing a mixture comprising a powder of cadmium sulfide, cadmium selenide, cadmium sulfoselenide or the like (starting material) and suitable amounts of an activator (a halide, sulfate or nitrate of gold, silver or copper), a coactivator (a halide such as ammonium chloride or the like, or a compound of a trivalent metal such as aluminum, gallium, indium or the like), a flux (a halide such as cadmium chloride, zinc chloride, sodium chloride, potassium chloride or the like), and a dispersant (sodium iodide, potassium iodide, sodium bromide, potassium bromide, sodium chloride, potassium chloride, sodium sulfate, calcium carbonate, sodium carbonate, calcium oxide or the like), whereby the degree of size of the growing crystals is controlled by the starting powder.

The activator used herein is a chemical which forms the acceptor level in the crystals of the starting cadmium sulfide or the like. The coactivator is a chemical which forms the donor level in the crystals of the starting cadmium sulfide or the like. Both the activator and the coactivator are to provide desired properties of the photoconductor. The flux is a chemical which has such property that in the firing step it melts at the firing temperature to fuse the starting powder. It should be understood that although the functions of the activator, coactivator and flux have been mentioned as above, sometimes a single chemical can perform two or three of the functions. The dispersant is a chemical which has such property that in the firing step, it neither melts at the firing temperature nor fuses the starting powder. The flux and the dispersant are distinguished from each other depending on the firing temperature. That is, depending on the firing temperature, there are the case where a substance is used as the flux and the case where the said substance is used as the dispersant. For example, sodium chloride which has a melting point of 800° C. is used as the flux when the firing temperature is more than 800° C., but may be used as the dispersant when the firing temperature is too low to melt the sodium chloride.

The dispersant used in the present invention has such property as mentioned above. One or two or more of such compounds may be used. The dispersant serves to divide the activated starting material into suitable fine units to inhibit the fusion and agglomeration of the starting particles. Further, the particle size of the resulting photoconductive powder is affected by the mixing ratio of the dispersant to the starting material and by the particle size of the dispersant. By selection of the dispersant, the particle size of the resulting photoconductive powder can suitably be controlled. Ordinarily, the dispersant is used in excess of the starting material.

It is desirable to use as the dispersant a substance having such properties that it is high in purity, has no chemical interaction with the starting photoconductive powder, is higher in melting point than the flux used, does not melt at the firing temperature, can disperse the photoconductive powder, and is water-soluble. For example, in case cadmium chloride is used as the flux, sodium chloride, potassium chloride, sodium bromide, potassium bromide, sodium iodide, potassium iodide, cadmium sulfate, zinc sulfate, sodium sulfate or potassium sulfate is preferable as the dispersant for the reasons that said compound is higher in melting point and lower in solubility in alcohols than cadmium chloride and hence can uniformly be dispersed by use of alcohol, and that it is water-soluble and hence can easily be separated, after firing, from the photoconductive powder by water-washing. The firing temperature in the present invention may be the firing temperature adopted in the known valence control method, and should suitably be selected in consideration of the kind of the starting material and the desired characteristics of the resulting photoconductive material.

The present invention is illustrated in further detail below with reference to examples.

EXAMPLE 1

A mixture comprising 175 g. of high purity cadmium sulfide of 0.5 to 1 micron in particle size, 50 g. of cadmium chloride as a flux, 6.4 g. of ammonium chloride as a coactivator, 15 cc. of an aqueous solution of 10^{-4} mole/cc. of copper chloride as an activator and 140 cc. of pure water was pulverized for 6 hours in an agate-made ball mill. Thereafter, the mixture was transferred to an evaporating dish and dried at 140° C. for about 15 hours. To the dried mixture were added 600 g. of sodium chloride as a dispersant and 400 cc. of absolute alcohol. The resulting mixture was pulverized for 6 hours in an agate-made ball mill. Thereafter, the mixture was placed in an evaporating dish and then dried at 120° C. for about 10 hours. The dried mixture was ground to the size of millet grains, and the resulting grains were charged into a quartz tube and then fired by use of an electric furnace in an air atmosphere at 590° C. for 15 minutes. After cooling to room temperature, the resulting brown fired substance was dipped in pure water, water-washed by decantation and then dried. The water-washing was terminated after repeating the decantation about 20 times to confirm that no chlorine ion had been detected in the waste liquid. The fired substance after drying was a brown crystalline powder of about 1 micron in particle size and showed photoconductivity. The particle size distribution of the thus obtained cadmium sulfide was measured by use of an optical microscope, and the percentage of the number of particles varying in size is shown in Table 1.

In this example, absolute alcohol is used for effective dispersion, but it is not always required to be used and may be replaced by another organic solvent. However, it is effective to use a solvent which is low in solubility for the dispersant.

EXAMPLE 2

Example 1 was repeated, except that an aqueous solution of 10^{-4} mole/cc. of $AgNO_3$ was used as the activator, KI as the flux and $CdSO_4$ as the dispersant, and the firing temperature was 700° C. The results obtained were as set forth in Table 1.

EXAMPLE 3

Example 1 was repeated, except that the amounts of the starting material, flux, activator, coactivator and dispersant used were varied as shown in Table 1. The results obtained were as set forth in Table 1.

EXAMPLE 4

Example 1 was repeated, except that cadium selenide was used in place of the starting cadmium sulfide, and the amounts of individual compounds used were varied as shown in Table 1. The results obtained were as set forth in Table 1.

EXAMPLE 5

Example 1 was repeated, except that the starting cadmium sulfide was replaced by cadmium sulfoselenide and the amounts of the individual components used were varied as shown in Table 1. The results obtained were as set forth in Table 1.

TABLE 1

	Example					Comparative Example		
	1	2	3	4	5	1	2	3
Starting material	CdS	CdS	CdS	CdSe	CdSSe	CdS	CdS	CdS.
Amount (g.)	175	145	175	48	180	180	180	180.
Flux	$CdCl_2$, 5/2 H_2O.	KI	$CdCl_2$, 5/2 H_2O.	$CdCl_{,2}$ 5/2 H_2O.	$CdCl_2$, 5/2 H_2O.	$CdCl_2$, 5/2 H_2O.	$CdCl_2$, 5/2 H_2O.	$CdCl_2$, 5/2 H_2O.
Amount (g.)	50	20	50	5.6	50	27.6	25	28.
Coactivator	NH_4Cl	NH_4Cl	NH_4Cl	NH_4Cl	NH_4Cl	NH_4Cl	NH_4Cl	NH_4Cl.
Amount (g.)	6.4	2.0	6.4	0.3	6.4	1.2	1.0	1.3.
Activator	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $Ag(NO_3)$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.	Aqueous solution of 10^{-4} mol/cc. of $CuCl_2$.
Amount (cc.)	15	3.5	15	3.0	15	2.2	1.2	0.12.
H_2O	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O.
Amount (cc.)	140	130	140	30	140	140	140	140.
Dispersant	NaCl	$CdSO_4$	NaCl	NaCl	NaCl	NaCl	NaCl	
Amount (g.)	600	200	550	100	400			
Particle size distribution (percent):								
0.5–1 μ	5	3	6	13	3			
1–2μ	93	22	91	83	95			
2–5μ	2	67	3	4	2	4		3.
5–10μ		8				24	23	33.
10–20μ						29	39	19.
20–30μ						29	26	29.
30–40μ						14	13	16.

In Table 1, there are also shown, for comparison, the results obtained by repeating Example 1, except that the dispersant was not used and the amounts of the individual components used were varied as shown in Table 1.

In order to enhance the sensitivity of the activated cadmium sulfide powder obtained in each of the above-mentioned examples, there may be effected the following treatments.

The crystalline powder after water-washing is mixed with 0.05 g. of cadmium chloride and 1.0 g. of ammonium chloride. The resulting mixture is dried at 140° C. for about 10 hours. Subsequently, the dried mixture is charged into a quartz glass tube and fired by use of an electric furnace in an air atmosphere at 590° C. for 15 minutes. The fired mixture, which has been taken out of the furnace after firing, is in such a state that crystalline particles, which are susbtantially in particle size with the particles before firing (about 1 micron), have slightly adhered to one another, and can be easily ground. After grinding in an agate-made mortar, the said soft fired mixture is packed in a quartz glass tube, and fired first in a hydrogen sulfide-nitrogen gas atmosphere at 500° C. for 10 minutes and then in a vacuum atmosphere at 500° C. for 10 minutes. Subsequetly, the first mixture is cooled to 100° C. in said vacuum atmosphere and then dried in a desiccator.

As is clear from Table 1, the photoconductive powder produced according to the present invention is composed of fine particles having a particle size within the range from 1 to 5 microns, and not only the particle size distribution thereof can freely be controlled by varying the blending amounts of the individual components (refer to Example 2) but also the fine particles are substantially in the form of spheres. Accordingly, when the photoconductive powder is formed into a photosensitive layer, the charging rate of the photosensitive material can be made greater.

In contrast thereto, the photoconductive powder produced according to any of the known processes (refer to comparative examples) is not only composed mainly of particles having a particle size within the range from 10 to 30 microns but also contains particles having a particle size of more than 30 microns, and shows a wide particle size distribution. Moreover, the particles are composed of spherical, rod-shaped and L-shaped particles.

The photoconductive powders prepared according to the aforesaid examples and comparative examples were subjected to sensitivity-increasing treatment. 5 grams of each of the thus treated photoconductive powders was dispersed in a mixture comprising 2 g. of an alkyd resin ("J–555" produced by Dai-Nippon Ink. Co.) and 2 g. of xylene. The resulting dispersion was coated on "comb type electrodes" (electrode distance 1 mm., length 150 mm.), which had been prepared by the vacuum deposition of aluminum onto insulating polyester films, and then dried and cured. Subsequently, a voltage of 100 v. was applied across the electrodes, and the amperes in the dark and the bright were measured by means of a microammeter. The results obtained were as set forth in Table 2 above.

TABLE 2

	Example			Comparative Example	
	1	2	4	1	2
Applied voltage (V)	100	100	100	100	100
Ampere (A) after allowing to stand in the dark for 15 min	2×10^{-13}	2.8×10^{-12}	2.8×10^{-10}	1.1×10^{-9}	1×10^{-10}
Ampere (A) after irradiation of 10 lux-light for 1 min	1.5×10^{-8}	6.2×10^{-9}	4.2×10^{-7}	4.8×10^{-4}	1.5×10^{-4}

From Table 2, it is understood that when a voltage is applied to "comb type photoconductive cells" prepared by use of the photoconductive powders according to the present invention, the dark and bright currents of the cells are far lower than in the case of cells prepared by use of the photoconductive powders according to the comparative examples, and the photosensitivities thereof are lowered.

In the case of the photoconductive powders according to the comparative examples, the voltage at which the cells had been damaged was 600 to 700 volts, whereas in the case of the photoconductive powders according to the present invention, said voltage was more than 2,000 volts. This is considered ascribable to the facts that the voltage applied had been consumed by a barrier layer derived from resistivity contact among the particles arranged between the electrodes, and that the uniformity of the photosensitive layer had been increased due to the use of finer photosensitive particles.

On the other hand, 5 g. of the photoconductive powder prepared in Example 1 was subjected to sensitivity-increasing treatment, and then dispersed in a mixture comprising 2 g. of alkyd resin and 2 g. of xylene. The resulting dispersion was coated on an aluminum plate and then dried and cured to prepare an electrophotographic light-sensitive plate having a sensitive layer of about 70 microns in thickness. The sensitive layer of said light-sensitive plate was electrically charged on the surface by use of a corona discharge electrode, to which had been applied a voltage of −6 kv., and then subjected to imagewise exposure for 0.2 second so that the bright portion became 30 luxes to form a static latent image. Subsequently, the latent image was developed with a toner according to an ordinary procedure and then transferred to a high quality paper, whereby a clear image free from fog was obtained.

Thus, even when used as an electrophotographic light-sensitive layer, the photoconductive powder obtained according to the present invention gives favorable results.

What we claim is:

1. A process for producing a photoconductive powder according to the valence control method comprising firing a photoconductive material selected from the group consisting of cadmium sulfide, cadmium selenide and cadmium sulfoselenide in the presence of an activator, a coactivator, a flux, and a particulate dispersant selected from the group consisting of sodium iodide, potassium iodide, sodium bromide, potassium bromide, sodium chloride, potassium chloride, sodium sulfate, calcium carbonate, sodium carbonate and calcium oxide at a temperature which is below the melting point of the dispersant but sufficient to melt the flux and introduce the activator and coactivator into the photoconductive material, wherein the amount by weight of dispersant is in excess of that of the photoconductive material.

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U.S. Cl. X.R.

96—1.5; 423—509, 561