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[54] **PROCESS FOR PRODUCING PHOTOCONDUCTIVE MATERIAL**
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ABSTRACT: A process for the production of a photoconductive powder, which comprises coating particles of a photoconductive material onto the surface of particles of a core material having an absorption ratio of less than 80 percent, at a thickness of 5 microns, to a light in the main region of the intrinsic sensitivity wave length region in which said photoconductive material exhibits a photoconductive property.

PROCESS FOR PRODUCING PHOTOCONDUCTIVE MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for producing a photoconductive material, and in particular, a photoconductive powder to by used for electrophotographic print marking processes.

2. Description of the Prior Art

As one of the modified electrophotographic processes, there has been proposed a process in which an image of photoconductive powder is formed on an electrically conductive or photoconductive support. In this process, a uniform layer of particles of photoconductive insulating powder, electrically charged, is placed on a support. Then, an imagewise exposure sufficient to decrease the electrical resistance of the powder is carried out on this powder layer, thereby forming an electrostatic latent image thereon according to the degree of the image density. In high image density areas, i.e., nonexposed areas, the residual potential of the powder layer is high and the electrostatic force between the support and the particles is relatively strong, whereas, on a sufficiently exposed area, the residual potential is low, resulting in a relatively weak electrostatic force between the support and the particles. Subjecting the thus processed layer to an external physical force, e.g., an air stream, electromagnetic force, or vibration of the layer, the powder particles with weakened electrostatic bonds are removed to form an image of powder particles in the areas with strong electrostatic bond.

It is well known to prepare photoconductive powders by finely dividing a solid of a mixture comprising particles of photoconductive powders dispersed uniformly in a suitable insulating resin, for example, by pulverizing. The sensitivity is generally so low that a clear image can hardly be obtained. This is possibly due to the fact that an increase in electrical conductivity, to correspond to the quantity of light radiated, is not sufficient in a layer under the powder layer, and the shape of the powder and other properties are not suitable.

A number of characteristics are required for a photoconductive powder to be used in the above-mentioned electric photographic print marking process. These are as follows: (1) high charging capacity, (2) low attenuation of the electrostatic potential of the charged particles in a dark place, (3) high sensitivity to light, (4) very low residual potential after exposure, (5) good powder-spreading and powder-removing properties, (6) free adhesive of bonding properties between the particles, and (7) spherical powder form. Moreover, the grain size is to be within a suitable range, since, although an image having a higher degree of resolution is obtained as the grain size gets smaller, a very small grain size impairs the powder-spreading and -removing property, that is, the flow property is lowered and adhesive properties appear. It is also required that the powder be scarcely affected by external conditions, such as, temperature and humidity, and the mechanical strength, in particular, friction resistance of the powder must be large. Other requirements are good fixing properties and suitable specific gravity, but after all, the most important factor is that the sensitivity to light be high, and the residual potential after exposure be low.

We have made efforts to obtain a photoconductive powder having such excellent characteristics, thereby leading to this invention.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a process for the production of a photoconductive powder, which is characterized by mixing a composition comprising photoconductive material and others, at least one of the components being in a vapor, solution or melt state, with such a powder that the absorption ratio is less than 80 percent at a thickness of 5 microns, to light in the main region of the intrinsic sensitivity wave length region wherein said photoconductive material has a photoconductive property, thereby adhering said composition to the surface of said powder. The photoconductive powder obtained by the invention differs completely from those commonly used in the prior art, particularly, in the fact that the photoconductive material is coated onto the surface of a powder of various organic and inorganic materials. A material to be coated preferably has a lower absorption to a light of the intrinsic sensitivity wave length region wherein a photoconductive material for coating has a photoconductive property. The photoconductive powder having such structure has such a low residual potential, after exposure, and such a high image contrast of latent image, in spite of its very sensitivity, small attenuation of electric potential in a dark place and high charging capacity, that a fog-free, sharp image can be obtained with a small exposure quantity. The other characteristics can all be satisfied, because a material having suitable shape, grain size and fixing property is used by selecting the material to be adhered.

As mentioned above, it is the principal object of the invention to provide a process for the production of a photoconductive powder having the foregoing structure in a very simple and economical manner.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the invention, a powder to be adhered, whose absorption ratio is less than 80 percent, at a thickness of about 5 microns, to a light in the main region of the intrinsic sensitivity wave length region wherein a photoconductive material has a photoconductive property, is kept in a stationary bed or fluidized bed using a suitable gas or liquid as a medium, or in a floated or suspended state, mixed with photoconductive material containing as at least one component a photoconductive material at least one component of which is in a vapor, solution or melt state, or in a dispersed state using a suitable gas or liquid as a medium by pouring, spraying, spreading, adding or the like, thereby to form a mixed system. The resulting mixture is fluidized, refluxed, stirred or kneaded adequately by an electromagnetic, thermal or mechanical external force to form a continuous film or fine spots of the covering material containing the photoconductive material around one or more powder particles. The photoconductive powder prepared by this method has very excellent characteristics.

It is important that the powder used as the material to be adhered is not markedly dissolved in, melted or etched by the adhering material, when the powder is stirred, mixed or kneaded therewith as a mixed system. Where there occurs a marked change, good characteristics cannot be obtained. However, if the powder is suitably swelled, surface-dissolved or surface-etched with at least one of the components of the mixed system, or mixed therewith, while being kept at a temperature sufficient to cause a suitable surface melting, or these take place simultaneously, the coating material is tenaciously bonded to the powder, resulting in a marked rise in mechanical strength, in particular, wear resistance, as well as in other characters.

Photoconductive insulating compounds investigated are, for example, selenium, cadmium sulfide, zinc oxide, or anthracene, while a nonphotoconductive powder to be bonded includes small beads of thermoplastic or thermosetting resins, glasses, inorganic salts, metal oxides, or other finely divided particles. They may be dyed or colored by suitable coloring matter, if desired.

These materials for nonconductive powder should be optically quite transparent to light in the spectrum region at which the photoconductive layer bonded thereon is sensitive. The transparency of the materials must be sufficiently high so that the less than 80 percent of the incident light is absorbed by the material when it is formed into a layer of 5 microns in thickness in the spectral region in which the photoconductive material is substantially sensitive.

In accordance with the process of the invention, photoconductive powder having very excellent electrophotographic characteristics, flowing properties, fixing properties, and mechanical strength can be produced in a very simple and economical manner by selecting and combining suitably a photoconductive material as a composing component, binding agent, solvent, medium material and powder material.

The present invention will now be illustrated by the following examples.

EXAMPLE 1

Photoconductive Zinc Oxide 150 parts (by weight)
Silicone Varnish (FSR—107: Trade Mark, manufactured by Fuji Polymer Industry Co., Ltd.) 60 parts
Cyclohexane 80 parts
Toluene 10 parts
Copper Stearate 0.2 part

The above compounds were mixed for 3 hours by the use of an attriter to prepare a photoconductive material. Then, 60 parts of the resulting dispersion was added to 100 parts of a vinyl chloride-vinyl acetate copolymer resin powder with 90 microns in average grain diameter, charged to a rotary kneader, then dried adequately by evaporating the solvent with warm air while stirring the mixture, and classified after pulverizing to give a photoconductive powder. The thus obtained photoconductive powder, having the foregoing characteristics, was favorable for the foregoing process.

EXAMPLE 2

Photoconductive Cadmium Yellow Orange 150 parts by weight
Silicone Varnish (KR—211 : Trade Mark, Manufactured by Shinetsu Chemical Industry Co, . Ltd.) 40 parts
Toluene 120 parts

These compounds were mixed or kneaded for 16 hours by the use of a ball mill of porcelain. Then, 40 parts of the resulting dispersion was added to 100 parts of polymethyl methacrylate powder having an average grain diameter of 90 microns, kneaded in a kneader and the solvent vapor was exhausted out of the system in a vacuum drier while continuing the kneading, thereby obtaining a photoconductive powder having favorable properties similar to those of Example **1**.

EXAMPLE 3

Photoconductive Zinc Oxide 200 parts by weight
Silicone Varnish (FSR—107: Trade Mark, Manufactured By Fuji Polymer Industry Co. Ltd.) 10 parts
Cyclohexane 175 parts
Toluene 15 parts
Methylethylketoxime 0.3 part

These compounds were kneaded for 16 hours by the use of a ball mill of porcelain. Then, 40 parts of the resulting dispersion was added to or sprayed over 100 parts of polyethyl methacrylate powder having an average diameter of 120 microns, and being fluidized, and dried by means of a rotary stirring apparatus while mixing and feeding warm air. A photoconductive powder was obtained without pulverizing and classifying. In this case, the surface of the polyethyl methacrylate powder was suitably swelled or surface-dissolved with the toluene in the dispersion, so a powder having a very excellent wear resisting property was obtained in spite of a small amount of the binding agent used.

EXAMPLE 4

Photoconductive Zinc Oxide 150 parts by weight
Silicone Varnish (ES-1001 Trade Mark, Manufactured By Shinetsu Chemical Industry Co. Ltd.) 40 parts
Diacetone Alcohol 150 parts
Amorphous Silica (Aerosil:Trade Mark, Manufactured By Degussa Co. Ltd.) 15 parts

The foregoing dispersion was sprayed against a polymethyl methacrylate powder to be cascade-spread in a proportion of 80 parts of 100 parts, continuously stirred with the feeding of warm air thereto, and the dried powder was taken out of the system.

EXAMPLE 5

Fine crystals of photoconductive zinc oxide and trichloroethylene heated at 120° C., to a vaporous state were dispersed in the air, circulated in an apparatus provided with a nozzle and refluxing means, and blown over a fluidized bed of methyl methacrylate-styrene copolymer powder maintained at a temperature lower than room temperature. The vapor of trichloroethylene condensed on the powder surface at a temperature lower than the dew point, and suitably swelled and resolved the powder surface, there thus being obtained a photoconductive powder wherein fine crystals of photoconductive zinc oxide were bonded uniformly and tenaciously to the thus varied surface.

EXAMPLE 6

In a cylindrical vacuum deposit apparatus, selenium vapor, heated to about 250° C., was ejected from a coaxial source towards the center of the cylinder. From the top end of the apparatus, the sufficiently cleaned transparent polymethylmethacrylate resin powder with an average grain diameter of 80 microns, which was heated to 60° C., was constantly flowed down along the axis of the cylinder. The powder particles were vacuum coated with selenium to give a high sensitive photoconductive powder.

The photoconductive powders prepared by the procedures of Examples show good characteristics. "Light" and "photoconductive property" used herein mean "light" in a broad sense, such as containing infrared ray, visible rays, ultraviolet rays, radiation and corpuscular ray, and "photoconductive phenomenon" in which the electric resistance is reduced by radiation thereof.

What we claim is:

1. A process for producing a photoconductive powder having high sensitivity and low residual potential and capable of providing clear electrophotographic images, said process comprising the steps of forming a suspension of particles of a core material in a fluid media, said core material having an absorption ratio of less than 80 percent, at a thickness of 5 microns, to a light in the main region of the intrinsic sensitivity wavelength region in which the photoconductive material exhibits a photoconductive property; contacting said particles of said core material while in suspension with a mixture of a photoconductive powder and solvent; maintaining said core material, photoconductive powder, and said solvent in suspension to effect intimate mixing thereof, continuing said mixing for a period of time sufficient for said solvent to dissolve the surface of said core material and until a continuous film of said photoconductive material is deposited onto the surface of the core material; effecting removal of said solvent from said fluid suspension to dry said coated core material, and recovering the resulting finely particulate product.

2. A process in accordance with claim **1** where said fluid media includes a binding agent for said core material and said photoconductive powder.

3. The process in accordance with claim **1** and further comprising forming a fluidized bed of said particles of the core material while maintaining said core material at a temperature lower than room temperature and contacting said fluidized bed of said core material with the vapors of said photoconductive powder and said solvent.

4. A process in accordance with claim **3** where said fluid media includes a binding agent for that core material and said photoconductive powder.