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[54] MANUFACTURING PROCESS FOR MANUFACTURING ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL

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[58] **Field of Search**.....96/1.5, 1.6, 1.7, 1.8, 108; 252/501

[56] **References Cited**

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[57] **ABSTRACT**

A process for manufacturing an electrophotographic sensitive layer which comprises adding a lead compound soluble in water and capable of generating lead ions upon dissolution in water and a water-soluble, sensitizing dye having a carboxyl group to a slurry prepared by dispersing a finely divided photoconductive zinc oxide in water thereby allowing the dye to be deposited fast on the surface of the zinc oxide so as to give rise to a colored zinc oxide powder, washing the powder with water, subsequently blending the colored powder which may be optionally mixed with untreated zinc oxide powder with an insulative resin, and spreading the resultant mixture in the form of a layer on a base having an electroconductive surface.

7 Claims, No Drawings

MANUFACTURING PROCESS FOR MANUFACTURING ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL

This invention relates to a novel electrophotographic sensitive layer. In obtaining a print by the electrofax process from the original of a color slide produced by using a silver halide photographic film, for example, the electrophotographic sensitive layer is required to have, as its property, photosensitivity over the whole visible range and gradation reproducibility of low contrast. The photosensitivity extending over the whole visible range is generally conferred upon by causing more than one kind of sensitizing dye to be adsorbed on the photoconductive material. Where zinc oxide is used as the photoconductive material, the resulting gradation reproducibility is generally of high contrast. In the case of a silver halide film, the gradation is accomplished by controlling the particle size distribution of silver halides to be used. In the electrophotographic process which uses a photoconductive material, however, it has been difficult to employ such means of gradation control. To be more specific, while it is possible to control gradation by regulating the distribution of the amount of sensitizing dye to be adsorbed on the photoconductive element, uniform adsorption tends to occur as a consequence of desorption and resorption of sensitizing dye in the course of sensitive layer production, making it difficult to achieve desired results.

Thus, an object of this invention resides in providing a manufacturing process for a zinc oxide insulative resin type electrophotographic sensitive material having excellent gradation reproducibility. Another object of the present invention consists in providing a satisfactory process for depositing a sensitizing dye fast onto zinc oxide particles.

The aforementioned objects of this invention have been accomplished by the discovery of a manufacturing process for an electrophotographic sensitive material, characterized by adding a lead compound soluble in water and capable of generating lead ions upon dissolution in water and a water-soluble dye possessed of carboxyl group to a slurry prepared by dispersing a finely divided photoconductive zinc oxide in water thereby allowing the said dye to be deposited fast on the surface of zinc oxide so as to give rise to a colored zinc oxide powder, washing the said powder with water, subsequently blending the colored powder (which may be mixed with untreated zinc oxide powder as occasion demands) with an insulative resin, and spreading the resultant mixture in the form of a layer on a base having an electroconductive surface. Since the aforementioned colored zinc oxide powder is such that the dye on zinc oxide is deposited with sufficient strength, separation of the deposited dye or re-adsorption to other zinc oxide occurs very seldom even when it is mixed with untreated zinc oxide. Therefore, there can be obtained an electrophotographic sensitive layer having low contrast of gradation reproducibility by mixing the aforementioned colored zinc oxide powder with untreated zinc oxide.

The dye to be used for the present invention contains carboxyl group and is easy to be deposited on zinc oxide. The dye which contains sulfonyl group is generally difficult to be deposited. Further, the lead ion which is utilized for the present invention has been found to have a higher capacity to deposit dye than other heavy metal ions. As compounds which donate such lead on, there are used water-soluble salts of lead nitrate, lead acetate, etc.

In the present invention, the reaction for depositing dye onto zinc oxide is carried out within a water dispersion. To be concrete, this is accomplished by preparing a slurry having zinc oxide sufficiently dispersed in water in advance and then adding into this dispersion of zinc oxide an aqueous solution containing therein a dye solution and lead ion. As a result of this treatment, the dye is insolubilized through combination with lead ion and consequently deposited fast on the surface of zinc oxide. At this time, the water slurry may be heated. The combination of dye and zinc oxide thus obtained is then washed sufficiently with water. This treatment of washing with water is aimed at removing water-soluble ion and therefore is important. In this treatment of washing with water, no removal of dye is observed at all so far as the procedure of this invention is concerned. Generally, a dye adsorbed onto zinc oxide is liable to come off upon washing. In the procedure of the present invention, however, the dye is deposited so fast that virtually no removal of dye occurs.

The colored, finely divided zinc oxide powder thus obtained is mixed with untreated zinc oxide as required and added into an insulative resin. By spreading the resultant mixture in the form of a layer on an electroconductive base, there can be obtained an electrophotographic sensitive material. The zinc oxide to be used for the purpose of this invention is manufactured generally by French process and has photoconductivity. The amount of dye to be used for this invention is in the range of from 0.0001 to 2 parts by weight based on 100 parts by weight of zinc oxide. In the case of this invention, a dye which is not adsorbed on zinc oxide in water can be used. That is to say, the dye to be used has only to satisfy the requirement that it should be deposited fast onto zinc oxide in the presence of lead ion.

In the following are given concrete examples of dye to be used for the present invention. It should be understood, however, that this invention is not limited thereto.

Eorsin, eriochrome cyanin R (color index 43,820), Chromazurol S (color index 43,825), alizarin violet (color index 45,445), phloxine (color index (acid red 98) 45,405), fluorescein, chrome pure blue (color index 43,830), chrome brilliant violet (color index 43,865), mordant brilliant red B (color index 45,305), chrome yellow GG (color index 14,025), chrome yellow M (color index 14,095), mordant blue 47 (color index 43,855). The dyes have invariably been observed to be deposited fast on zinc oxide and to manifest sensitizing activity. A sensitive layer with good gradation reproducibility can be produced by using the colored zinc oxide of this invention alone. By using the colored zinc oxide to be obtained as mentioned above in combination with untreated zinc oxide, there can be obtained a sensitive layer having still better gradation reproducibility of low contrast. In this case, the colored zinc oxide is mixed at a ratio of 0.1 – 5 parts by weight with 1 part by weight of untreated zinc oxide.

The present invention is described in further detail below by referring to working embodiments thereof.

EXAMPLE 1

In a glass beaker, 10 g. of photoconductive zinc oxide (made by Sakai Chemical Co., Ltd.) was placed and stirred with 200 ml. of distilled water added thereto. Then the mixture was subjected to ultrasonic waves at 29 KHz. to afford a water dispersion of sufficiently distributed zinc oxide. To this dispersion was added 5 ml. of 0.1 percent aqueous solution of eosin. Eosin was not appreciably adsorbed out of the aqueous solution onto zinc oxide. When 5 ml. of 1 percent aqueous solution of lead acetate was added to thereto, however, eosin was observed to be adsorbed abruptly onto zinc oxide. When zinc oxide was separated from the mother liquor by means of a centrifugal separator, the mother liquor became substantially colorless and clear, suggesting that eosin had been adsorbed completely onto zinc oxide. The zinc oxide now in peach color was again dispersed in 100 ml. of distilled water. Eosin was not observed to separate from the surface of zinc oxide. Again, zinc oxide was collected. When the zinc oxide in peach color was washed sufficiently with methanol, eosin was not observed to separate into the mother liquor. The zinc oxide was dried and then combined with 2 g. of vinyl chloride-vinyl acetate copolymer and 13 g. of butyl acetate and sufficiently blended in a small ball mill. The resultant paste in peach color was spread on an aluminum plate. The dry thickness of the layer was 6.5μ. The layer was dried and thereafter allowed to stand for 10 hours in a dark room kept at 40° C. The sensitive layer thus obtained was found to acquire an electric potential of −360 V upon negative corona discharge. It was exposed to light projected through an optical wedge and subsequently

developed with a liquid developing agent containing therein a positively charged toner. The value "γ" indicating gradation was 1.1. Test of spectroscopic sensitivity showed that the sensitive layer had been sensitized in the spectrum range of 480–560mμ.

EXAMPLE 2

By using 2.5 g. of the zinc oxide in peach color obtained in Example 1 and 7.5 g. of untreated zinc oxide and following the procedure of Example 1, there was prepared a sensitive layer. The value "γ" indicating the gradation of this sensitive layer was 0.7.

EXAMPLE 3

The procedure of Example 1 was followed, except Chromazurol S (mordant blue 29, color index 43825) was used in the place of eosin. Thus was obtained zinc oxide powder in bluish purple color. When a sensitive layer was prepared from this powder, the layer was found to be sensitized throughout substantially whole visible range.

EXAMPLE 4

A sensitive layer was prepared by following the procedure of Example 1, except lead nitrate was used in the place of lead acetate. The layer gave virtually the same results.

What is claimed is:

1. A process for manufacturing an electrophotographic sensitive layer which comprises adding a lead compound soluble in water and capable of generating lead ions upon dissolution in water and a water-soluble sensitizing dye having a carboxyl group to a slurry prepared by dispersing a finely divided photoconductive zinc oxide in water thereby allowing the said dye to be deposited fast on the surface of zinc oxide so as to give rise to a colored zinc oxide powder, washing the said powder with water, subsequently blending the colored powder with an insulative resin, and spreading the resultant mixture in the form of a layer on a base having an electroconductive surface.

2. The process as claimed in claim 1 wherein the lead compound is lead acetate or lead nitrate.

3. The process as claimed in claim 1 wherein the amount of the dye to be used is in the range of from 0.0001 to 2 parts by weight based on 100 parts by weight of zinc oxide.

4. The process as claimed in claim 1 wherein the amount of the lead compound to be used is in the range of from 0.0005 to 5 parts by weight based on 100 parts by weight of zinc oxide.

5. The electrophotographic sensitive layer manufactured by the process as claimed in claim 1.

6. The process as claimed in claim 1 wherein said dye is Eosine, Eriochrome cyanine R, Chromazural S, Alizarin violet, Phloxine, Fluorescein, Chrome pure blue, Chrome brilliant violet, Mordant brilliant red B, Chrome yellow GG, Chrome yellow M or Mordant blue 47.

7. A process as in claim 1 where said colored zinc oxide powder is mixed with untreated zinc oxide powder.

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