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Honjo et al.

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[54] **METHANOL AND HEAT TREATED ZINC OXIDE**

[75] Inventors: **Satoru Honjo; Hajime Miyazuka,** both of Asaka, Japan

[73] Assignee: **Rank Xerox, Ltd.,** London, England

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **G03g 5/02,** G03g 5/08

[58] **Field of Search** 96/1.8; 252/501; 23/147, 23/148

[56] **References Cited**

UNITED STATES PATENTS

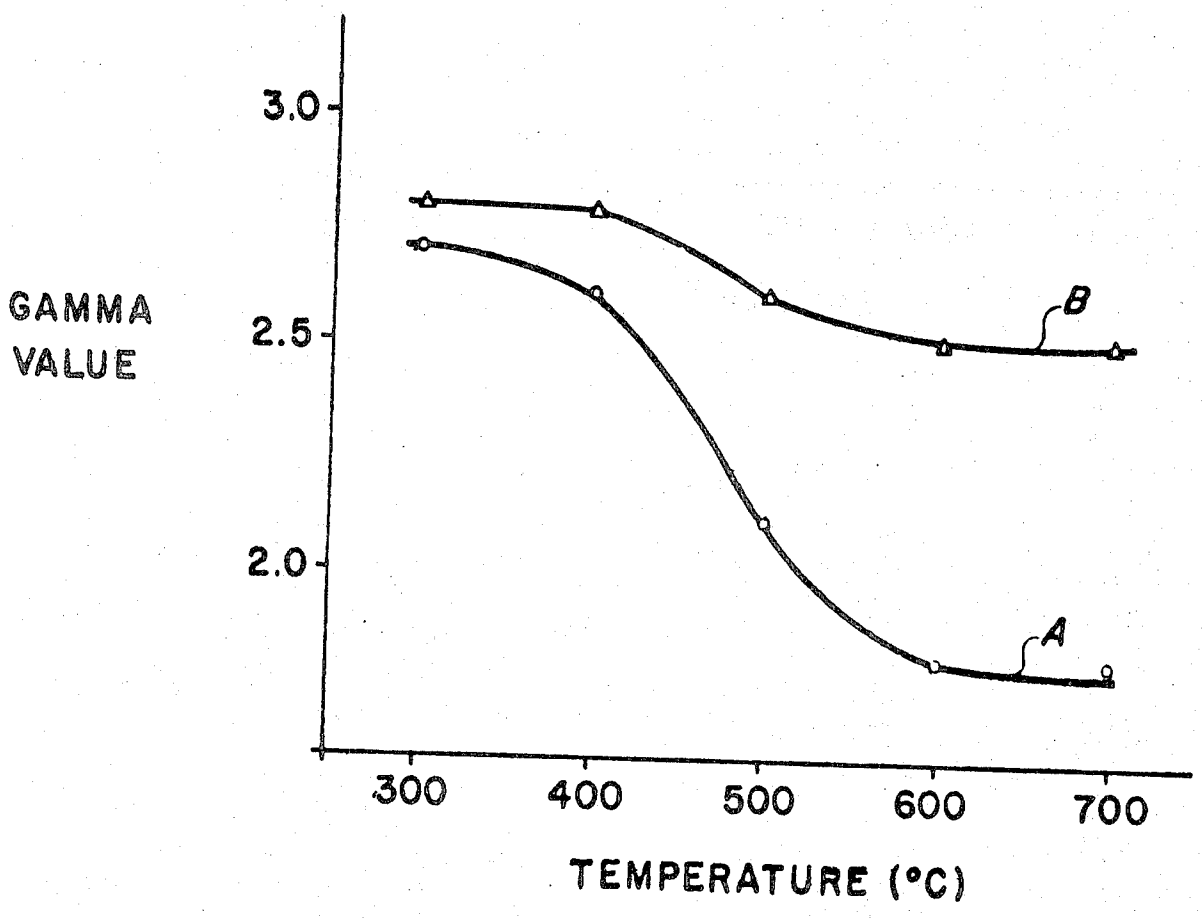
3,089,856	5/1963	Cyr et al.	252/501 X
3,429,662	2/1969	Klein	96/1.8 X
3,538,022	11/1970	Bowman	23/147 X

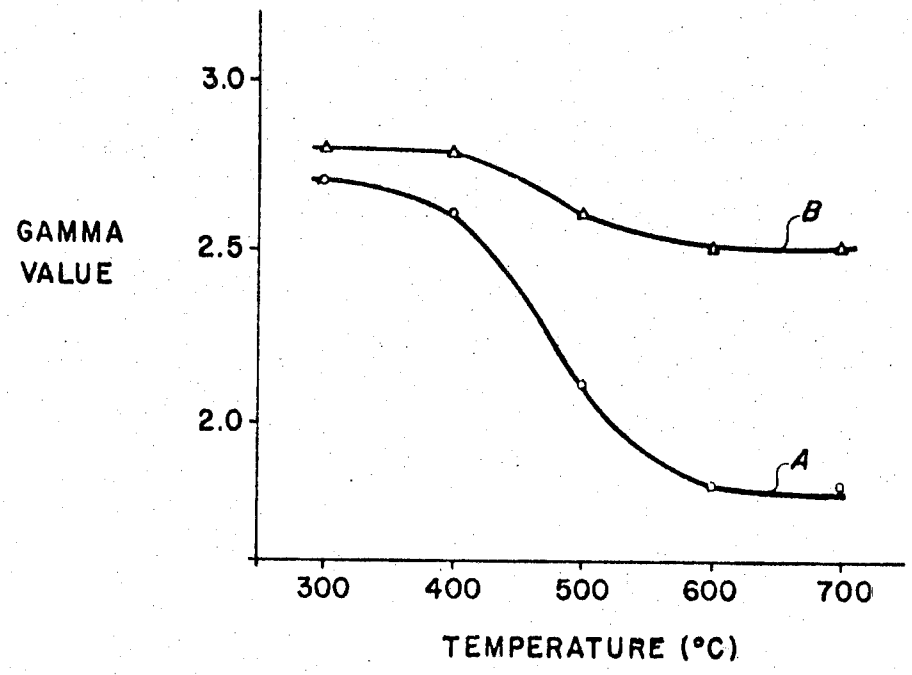
Primary Examiner—Roland E. Martin, Jr.

[57] **ABSTRACT**

Photoconductive zinc oxide powder is wetted with a liquid selected from the group consisting of water, methanol and mixtures thereof and thereafter heat treated at a temperature between about 400° and about 700°C. The treated zinc oxide powder may be mixed with a resinous binder and thereafter formed into an electrophotographic layer.

1 Claim, 1 Drawing Figure




GAMMA VALUE
3.0
2.5
2.0
B
A
300
400
500
600
700
TEMPERATURE (°C)

METHANOL AND HEAT TREATED ZINC OXIDE

BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more particularly, to a method for forming improved photoconductive materials.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. One conventional process involves placing a uniform electrostatic charge on a photoconductive insulating layer comprising zinc oxide powder and a resinous binder carried on a conductive paper substrate, exposing the layer to a light-and-shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting electrostatic latent image by depositing on the image a charged toner which is usually dispersed in an insulating liquid. The charged toner may be suitably colored and may have a polarity of charge identical or opposite to that of the latent image to be developed.

Generally, photoconductive insulating layers comprising zinc oxide powder and a resinous binder exhibit poor continuous tone characteristics. This is unlike conventional silver halide emulsion photographic layers in which various characteristics extending from soft tones to hard tones, e.g. No. 1 to No. 5, are readily available. In graphs in which the logarithm of exposure along the abscissa is plotted against retentive potential or developed density along the ordinate photoconductive layers containing zinc oxide powder and an insulating film-forming binder are characterized by curves having a short linear portion and a long steep hard tone portion. Generally, this characteristic of the zinc oxide binder layer cannot be modified to any great extent by changing the ratio of the binder and the zinc oxide photoconductor material or by altering blending conditions therefore.

Techniques have, however, been reported which regulate the reproduction scale of electrophotographic photosensitive layers. These techniques include the technique described in Japanese Patent Application publication 11710/66 in which the photosensitive layer is prepared by blending non-sensitized zinc oxide, dye-sensitized zinc oxide and binder material; the technique disclosed in U.S. Pat. No. 3,003,870 in which a dot pattern containing zinc oxide photosensitive material of one photosensitivity is formed on a continuous layer containing zinc oxide of a different photosensitivity; and the technique disclosed in British Patent No. 967,690 in which a polarity of photosensitive layers dye-sensitized to different degrees are superposed upon each other. These techniques unfortunately are accompanied by serious drawbacks. For example, in applying multiple layers of photosensitive materials or in applying a single layer containing non-sensitized zinc oxide and dye-sensitized components, redistribution of sensitizing dye from dye-sensitized to non-sensitized zinc oxide frequently occurs and markedly reduces any improvement in the ability of the resulting photosensitive member to reproduce continuous tones.

SUMMARY OF THE INVENTION

It is therefore, an object of this invention to provide an electrophotographic photosensitive material overcoming the abovenoted deficiencies.

It is another object of this invention to provide an electrophotographic photosensitive material having

"soft" characteristics suitable for the reproduction of continuous tone images.

It is a further object of this invention to provide an electrophotographic photosensitive material which forms continuous tone reproductions with liquid developers.

It is still another object of this invention to provide an electrophotographic photosensitive material superior to those of known electrophotographic photosensitive material.

The above objects and others are accomplished by wetting zinc oxide particles with water, methanol or mixtures thereof and thereafter subjecting the zinc oxide particles to a heat treatment at a temperature between about 400° and 700°C. The resulting treated zinc oxide may then be mixed with a resinous binder to form an electrophotographic photosensitive layer.

BRIEF DESCRIPTION OF THE DRAWING

The advantages of the improved electrographic photosensitive material of this invention will become even further apparent upon consideration of the following disclosure of the invention, particularly when taken in conjunction with the accompanying drawing wherein the variation of the gamma value characteristics of electrographic photosensitive materials are illustrated with respect to temperature of thermal treatment for the zinc oxide particles employed therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment, the principle zinc oxide treatment steps of this invention include a uniform dispersion step, a drying step and a heating step. In the uniform dispersion step, zinc oxide powder produced by conventional techniques such as the gaseous oxidation process is uniformly dispersed in water, methanol or a mixture thereof. Zinc oxide powder is readily dispersible in water or methanol, particularly in the latter, and forms a substantially homogeneous dispersion.

In the drying step, the solid phase is separated from the dispersion and the resulting paste is dried to remove the dispersing liquid.

The dried zinc oxide particles are then heat treated at a temperature between about 400° and about 700°C. Any suitable heating device such as an electric furnace may be employed. The heat treatment step is usually effected for at least about 30 minutes in an oxidative atmosphere, preferably an atmosphere of air or oxygen.

In another embodiment of this invention, the drying step and the heating step described above are carried out simultaneously. However, it is preferred to conduct the drying step prior to the heating step, particularly when a mixture of water and methanol are employed. The water content present on the surface of powdered zinc oxide particles treated with a mixture of water and methanol and thereafter subjected to a drying step usually changes in relation to the ratio of water in the water-methanol mixture employed in the uniform dispersion step. Since zinc oxide is easily wetted by and dispersed in a mixture of water and methanol, water is more uniformly distributed on the surface of zinc oxide particles after the drying step.

The conditions of the drying step are not especially critical and considerable latitude is permitted as to the drying temperature or drying time employed. Gener-

ally, adequate removal of dispersing liquids is achieved with drying temperatures less than about 150°C.

Undesirable effects in the crystal lattice structure usually occurs when a heating temperature exceeding about 700°C is employed. These undesirable effects are accompanied by a deterioration of the characteristics of the photosensitive layer formed from the treated zinc oxide particles. More specifically, the photosensitivity of the photosensitive layer is adversely effected. In addition, high heating temperatures will cause sintering of the zinc oxide particles thereby forming agglomerates which are undesirable in photoconductive layers containing zinc oxide particles dispersed in a resinous binder. Thus, the temperature of the heat treating step is preferably maintained at a temperature less than about 700°C.

Electrophotographic photosensitive members are formed with the zinc oxide powder of this invention by uniformly dispersing the treated zinc oxide particles in an insulating film-forming binder. The resulting dispersion may be applied to an electrically conductive surface. Any suitable resin binder conventionally employed as binders for zinc oxide photoreceptors may be employed with the treated zinc oxide dispersion technique may be employed to disperse the zinc oxide particles in a resinous binder. If desired, the spectral sensitivity of the treated zinc oxide particles of this invention may be increased by treating the zinc oxide particles with conventional sensitizing dyes. Electrophotographic photosensitive layers formed with the treated zinc oxide particles of this invention are characterized by excellent dark-decay properties and low gamma values. Thus, curves formed by plotting the logarithm of exposure along the abscissa against the retentive potential or developed density along the ordinate will exhibit decreased steepness for electrophotographic photosensitive layers containing the treated zinc oxide particles of this invention. It is unlikely that these two characteristics, low gamma value and excellent dark-decay behavior, are simultaneously attained with the prior art methods for producing photosensitive materials.

Although the gamma value of zinc oxide particles may be reduced slightly by eliminating the uniform dispersion and drying steps described above, the reduction is substantially less than that achieved by utilizing all the steps in accordance with the process of this invention.

The characteristics of the electrophotographic photosensitive layer, particularly the gamma value thereof, appears to depend greatly upon the water content in the solids after the drying step. More specifically, the gamma value decreases with an increase in water content. However, a marked deterioration of dark-decay characteristics are observed when the water content in the zinc oxide powder particles exceeds 20 percent by weight. It has been found that the water content in the zinc oxide powder may be adjusted by any suitable technique such as by regulating the relative quantity of water in the water-methanol mixture described above, the temperature employed in the drying step, the drying time and the like.

Thus, preselected low gamma values for electrophotographic photosensitive layers containing the treated zinc oxide particles of this invention may be achieved by regulating the water content of the zinc oxide particles prior to the heat treatment step. The water content of zinc oxide particles may be regulated by other wetting techniques. However, other wetting techniques such as maintaining zinc oxide powder in an atmosphere of high temperature and high humidity or flowing water vapor or humid gases through a layer of zinc oxide powder require complex equipment and process steps as well as special heating apparatus to obtain powder having a uniformly distributed water content. Thus, accurate control of the water content of treated zinc oxide particles is most accurately and uniformly achieved with the uniform dispersion step of this invention.

Surprisingly, a reduction of gamma values is not achieved at any water content, with or without the drying step described above, when the heat treating step of this invention is omitted. In other words, marked reduction of gamma value characteristics is achieved only when the uniform dispersion step, drying step and heating step (the latter two steps being optionally combined) are employed to treat zinc oxide particles.

The gamma value of the treated zinc oxide photoreceptors of this invention also appear to be affected to some extent by the drying step in which the paste of dispersing liquid and zinc oxide powder is dried. Suitable selection of drying conditions in the drying step will provide zinc oxide particles having a water content lower than that in untreated zinc oxide particles. Electrophotographic photosensitive layers prepared with treated zinc oxide particles having a lower water content than that found in untreated zinc oxide particles unexpectedly exhibit a lower gamma value than electrophotographic photosensitive layers prepared with untreated zinc oxide particles having a higher water content than the treated zinc oxide particles. It is hypothesized that the reduced gamma value may be due to the recrystallization of ions dissolved in the dispersing liquid during the drying step whereby some zinc oxide particles adhere to each other.

As described above, the treated zinc oxide particles of this invention may be dye sensitized with many conventional dye sensitizors. However, zinc oxide particles treated by the technique of this invention may lose their affinity to some dyes such as erythrosine. Thus, reduced sensitization may be observed with dyes which are poorly absorbed by the treated zinc oxide particles.

The following examples further define and compare and describe preferred embodiments and materials of the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

About 200 parts zinc oxide powder (Saze × 2000, Sakai Kagaku Company) is dispersed in a mixture of about 640 parts of methanol and about 200 parts water and subjected to ultrasonic wave energy to obtain a homogeneous dispersion of zinc oxide. A paste containing the zinc oxide powder and dispersing solvent is obtained by centrifugal separation of the uniform dispersion. The paste is dried in a drying chamber at about 50°C for about 16 hours. Upon completion of the drying step, the dried zinc oxide powder is heated in a Mackel type electric furnace. The temperature in the furnace is increased at a rate of about 4°C per minute and thereafter heated at a constant temperature for about 2 hours in a quiescent atmosphere. The constant temperatures selected are 300°, 400°, 500°, 600°, and 700°C. About 100 parts of the resulting treated zinc oxide powder is mixed with about 60 parts of styrene-

alkyd resin solution (Styrenezol 4400, Japan Reichold), about 40 parts of polyisocyanate solution (Desmodule L, Bayer) and about 130 parts of butyl acetate-xylol (1:1) mixture. After blending in a homogenizer for about 10 minutes, the mixture is applied as a coating onto aluminum foil laminated to paper. Sufficient coating material is deposited to form a dry and hard coating having a thickness of about 5 to about 6 microns subsequent to heating for at least about 15 hours at about 50°C. The thus prepared electrophotographic photosensitive member is cut into test samples and stored in the dark for 2 days. Some of the test samples are tested for light-decay characteristics by exposing the samples to tungsten lamp light sources of different illuminance. The rate of potential retention is calculated with the following formula: $(V_L/V_o/v_D/V_o \cdot) \times 100\%$ wherein V_o, $V_o \cdot$, V_L and V_D respectively represent potentials prior to exposure, prior to dark-decay measurements, seven seconds after exposure for a fixed period to a light of illuminance 1 and 7 seconds after the start of dark decay. The characteristic curve is obtained by plotting the potential retention rate along the ordinate and log 1/It along the abscissa. A length of 100 in ordinate is equal to 20 in abscissa. Two parallel straight lines having a distance therebetween of 0.1 measured by the log 1/It are drawn so as to position the above-described curve therebetween. The slope of these lines are taken as the gamma value.

The attached drawing illustrates the behavior of gamma value of an electrophotographic photosensitive layer as the temperature of heat treatment is changed. The behavior observed in electrophotographic photosensitive layers containing zinc oxide particles treated according to the process of this invention (curve A) is compared to electrophotographic photosensitive layers containing zinc oxide heated without the dispersion and drying steps of this invention (curve B). As shown in the drawing, the reduction of gamma value with an increase in temperature of heat treatment is more pronounced with the zinc oxide powder treated by the process of this invention and becomes particularly apparent when the temperature of heat treatment is equal to or greater than about 500°C.

EXAMPLE II

The procedure of Example I is repeated except that the ratio of water and methanol is altered to obtain zinc oxide particles having various water contents. The heating step is conducted at about 600°C for about 2 hours. The water content in the zinc oxide particles after the drying step as well as the accompanying change of gamma value in an electrophotoconductive photosensitive layer prepared with the treated zinc oxide particles is illustrated in the following table. For purposes of comparison, the gamma value obtained with zinc oxide powder not subjected to the uniform dispersion and drying steps is listed in the following table. As shown in the following table, the gamma value decreases with an increase in water content thus indicating the advantages of this invention over prior art processes in obtaining low gamma values.

WATER CONTENT	GAMMA
0.18% (untreated)	2.5
0.16%	2.1
0.20%	2.0
1.50%	1.9
10.9%	1.4

As described above, the water content in the zinc oxide particles after the drying step as well as the gamma value of photosensitive layers obtained with the zinc oxide particles (heated at 600°C for about 2 hours) are listed in the table shown above.

EXAMPLE III

About 1000 parts zinc oxide particles are dispersed in about 4000 parts of water and processed as described in the foregoing Examples. The zinc oxide particles are heated for 2 hours at 500°C. About 700 parts of the resulting treated zinc oxide powder is dispersed in about 50 parts of styrene-alkyd resin solution (Styrezol 4400, Japan Reichold) in a porcelain ball mill for about 10 hours. The ball milled dispersion is then mixed with about 50 parts polyisocyanate hardener solution (Desmodule L, Bayer) and sensitizing dye solution containing about 0.14 parts of edible blue dye No. 1, about 0.28 parts of eosin and about 0.35 parts of fluorescein in a mixture of about 10 parts of water and about 50 parts of ethanol. The resulting mixture is thoroughly blended for about 20 minutes. The blended mixture is coated onto a substrate and tested as described in Example I. The photoconductive binder plate containing the treated zinc oxide particles exhibits satisfactory soft characteristics with a gamma value of about 1.4.

Although specific materials and conditions are set forth in the foregoing Examples, these are merely intended as illustrations of the present invention. Various other suitable relative quantities of water, methanol or mixtures thereof, drying conditions, heating conditions, conventional zinc oxide photoreceptor resinous binders, sensitizing dyes and the like including those listed above may be substituted for those in the specific Examples with similar results. Other materials may also be added to the zinc oxide powder or zinc oxide binder plate to sensitize, synergize or otherwise improve the imaging properties or other desirable properties of the system.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A process for treating photoconductive zinc oxide powder comprising the steps of wetting zinc oxide powder with methanol and thereafter heat treating said zinc oxide at a temperature between about 400°C and about 700°C in an oxidative atmosphere.

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