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METHOD OF PRODUCING ELECTROPHOTOGRAPHIC COATINGS

Satoru Honjo and Hajime Miyatuka, Asaka, Japan, assignors to Fuji Photo Film Co., Ltd., Nakanuma, Minami-Ashigara Machi, Ashigara-Kamigun, Kanagawa, Japan

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ABSTRACT OF THE DISCLOSURE

Prior to blending with a resin binder, an inorganic photoconductive powder is wetted with an organic solvent having a strong dissolving power such as ketones, pyridines, benzaldehyde, nitrobenzene, ethylenediamine, etc. By virtue of the pretreatment of the photoconductive powder, the period for blending with a resin binder solution is remarkably reduced, and the resulting coating exhibits a high sensitivity to light with an improved surface smoothness. The coating is especially suited for liquid development. This invention is an improvement of the method described in British Patent No. 1,067,116.

This invention concerns a process for the production of photoconductive compositions for use in preparing electrophotographic coating.

An electrophotographic coating employed in the typical electrophotographic process which comprises uniform charging, imagewise exposure, and toner development of a photoconductive coating is usually produced by homogeneously dispersing a photoconductive powder such as zinc oxide, cadmium sulfide, or titanium dioxide, in an insulating film-forming binder thorough blending and then coating the mixture on a suitable conductive support. The blending of the photoconductive powder and the resin binder is usually carried out with the use of ball mill, sand grind mill and other dispersing means. The time for blending is determined by the surface smoothness of the resulting coating formed from the blended mixture. The surface must be sufficiently smooth so that a toner image obtained shows an acceptable level of uniformity.

When the blending is insufficient, the inorganic photoconductive powder cannot be divided into minute particles having sufficiently small particle diameters instead a large number of large agglomerates remain which are easily observed in the resulting coating. Such spots due to the agglomerates differ in electrophotographic properties from the surrounding uniform areas, thus bringing about mottles in image density or forming white spots in the developed solid image to noticeably deteriorate image resolution. The time required for blending also depends to a great extent on the particle size of the photoconductive powder involved.

Generally speaking, larger particles are more difficult to disperse thus requiring a longer or more intense blending. For example, zinc oxide having an average particle diameter of 0.5 micron requires at least 6-hour ball milling though this value varies by the diameter of the mill, the size of the balls, and the amount of the zinc oxide charged in the mill. With coarser zinc oxide of more than 1 micron blending for more than 10 hours is necessary.

An excessive blending, however, causes destruction of the primary particles and introduces undesirable irregularities in the crystal lattice of the photoconductor, which seriously deteriorates the photoconductive properties of the obtained photoconductive coating. Accordingly, a prolonged blending must carefully be avoided. As the blending is continued, the surface of the photoconductive

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powder particles is wetter with the resin binder, which also causes lowering of the light-sensitivity of the photoconductive coating.

It is also a well-known empirical fact that an electrophotographic coating comprising a coarser photoconductive powder exhibits a higher light-sensitivity. Considering all the above-mentioned facts, it will be evident that the surface smoothness and the sensitivity conflict with each other as for an electrophotographic coating.

That is, to obtain a high sensitive coating, one must lower the surface smoothness to some extent, and vice versa.

The major factor to determine the surface smoothness is the degree of dispersion of the photoconductive powder in the coating. The more minutely the powder is dispersed, the smoother the surface becomes. It should be noted that ordinary film-forming resin binders are dissolved in toluol or xylol which have poor wetting power for many inorganic photoconductive powders. Another important factor dominating the light sensitivity of the electrophotographic coating is the ratio of the resin binder to the photoconductor. A higher content of the photoconductive powder is preferable as for light sensitivity.

Thus, in order to produce an electrophotographic coating having an acceptable surface smoothness as well as a high photoconductive response, it will seem promising to eliminate or decrease direct contact of the photoconductive powder with the resin binder in the coating and, at the same time, realize a minute and uniform dispersion of the photoconductive powder.

A method is proposed, to attain the present object, in Japanese patent publication No. 13,516/68, which comprises prior to blending zinc oxide and a binder the zinc oxide is milled in the presence of an organic liquid selected from glycol, glycol ether (monoalkylether) or anhydrous alcohol which readily wet the zinc oxide surface and decompose into minute particles.

Though this method has proved quite effective to essentially solve the above difficulty, it cannot be applied for formulations which are incompatible with the above mentioned fluidizing agents (glycol glycol ether, etc.). For example glycols, glycol ethers (monoalkyl ethers) or alcohols having high boiling points cannot be incorporated in binder formulations which utilize polyisocyanate compounds as curing agent for alkyd, epoxyster, or epoxide resins, since hydroxyl-containing solvents will deteriorate the electrophotographic properties of the resulting coatings. Moreover, many resin binders suitable for electrophotographic coating are usually dissolved in nonpolar solvents such as toluol or xylol and insoluble in polar solvents. And these nonpolar solvents are generally more volatile than glycols or other polar fluidizing agents mentioned above. When there is applied a coating mixture containing a photoconductive powder wetted with a polar fluidizing agent and a binder dissolved in a nonpolar volatile solvent, the nonpolar solvent will evaporate first. As drying proceeds, a point will be reached when the resin binder separates out of the solution due to the change of the solvent composition. The coating thus prepared often exhibits poor mechanical strength and low uniformity.

To avoid this problem by making use of the process described in Japanese patent publication No. 13,516/68, substitution of the fluidizing solvent such as glycol is necessary, for example by removing the supernatant liquid separated by the centrifuge of the fluidized zinc oxide, and further washing with harmless solvent. Such additional processes will raise the manufacturing cost of the electrophotographic recording material unreasonably and are inadequate for industrial scale.

Organic solvents used as fluidizing agent in the said patent must have a high affinity with the inorganic photoconductive powders, and those having hydroxyl groups in

the molecular structure such as alcohols, and glycol ethers (monoalkylether), are known to remarkably wet the surface of many inorganic photoconductive powders such as zinc oxide, cadmium sulfide, or titanium dioxide. This indicates that the hydroxyl radical has a strong interaction with the surface of these powders.

Our experiments have disclosed that an important factor determining the wettability of an organic solvent as for inorganic photoconductive powders is, besides the hydroxyl group in the molecular structure, a relatively high dielectric constant with a lower limit of about 10 at 20° C. In other words, organic solvents free of hydroxyl group can also wet the surface of inorganic photoconductive powders provided that they have dielectric constants greater than the above-mentioned value. Those accomplishing this object include acetone, methylethyl ketone, diethylketone, isobutyl ketone, methyl-n-propyl ketone, cyclohexanone, benzophenone, or other ketones, pyridine, benzaldehyde, nitrobenzene, ethylenediamine, etc.

Since these solvents can dissolve many organic resin binders which are suitable for electrophotographic coating for liquid development, they need not be removed at subsequent steps.

When an inorganic photoconductive powder such as zinc oxide is immersed in toluene, or xylene which is the most prevailing solvent for binders of electrophotographic coatings, the powder would not disperse therein, instead would form a structure due to aggregation and a homogeneous mixture would never be gotten.

On the contrary, solvents having a high dielectric constant such as acetone have proved to readily wet the surface of inorganic photoconductive powders, and form a uniform dispersion without causing separation between the solid and liquid phases.

The object of the present invention is to disclose a method of producing an electrophotographic coating comprising an inorganic photoconductive powder and an insulating film-forming resin binder suited for liquid development and having a high sensitivity to light as well as an improved surface smoothness.

Another object of the present invention is to realize the shortening of the time required for the manufacture of an electrophotographic coating.

The above object can be accomplished by treating an inorganic photoconductive powder prior to blending with an insulating film-forming resin binder with an organic solvent having dielectric constant greater than 10 at 20° C. and a high dissolving power and free of hydroxyl group (typical examples are ketones such as acetone, and methylethyl ketone), then blending the binder and the thus treated photoconductive powder in a relatively brief period, obtaining a uniform coating mixture, and coating the mixture on a suitable conductive substrate to form an electrophotographic material. An important advantage of the present method is that it is compatible with a wider variety of resin compositions. The pre-treatment may be carried out by any type of dispersing apparatus such as ball mill, sand mill, or colloid mill, or by an emulsifier such as homogenizer or homoblender. In some instances the pre-treatment may be enhanced by incorporating into the pre-treating solvent a resinous material as much as 1-25% of the weight of the photoconductor involved or a suitable amount of surface-active agent. The time for pre-treatment may be about a half to two hours for ball milling, and a half to one hour for homogenizer, though it depends on the amount of photoconductor charge and the average particle diameter thereof.

In the case of a blender such as ball mill or sand grinding mill which employs a dispersing medium such as porcelain ball or Ottawa sand, a prolonged blending of the photoconductive powder must be carefully avoided since it will cause crushing of the primary particles of the photoconductive powder or introduce lattice defects in the crystal structure which brings about a considerable decrease of the light sensitivity. Excessive grinding can

be detected by the yellowing of the powder in the case of zinc oxide or titanium dioxide.

Blending of the pre-treated photoconductor with an insulating film-forming resin binder must be completed and form a uniform dispersion as briefly as possible. For this purpose, an emulsifying apparatus such as homogenizer or homomixer is not suitable, the optimum dispersing condition being around 5 to 10 minutes at 10,000 to 15,000 r.p.m. From a dispersion thus prepared an electrophotographic coating results in which the photoconductive powder is finely divided and at the same time does not contact with the resin binder, showing a high sensitivity to light as well as an acceptable smoothness of the surface.

When spectral sensitizers are to be incorporated in the electrophotographic coating, they may be added either at the pretreatment or blending operation. In the former case, it should be noted the sensitizers are susceptible to mechanochemical effect to lose their sensitivity, and therefore an over-grinding in a ball mill or sand grind mill should be avoided.

The preparation for an electrophotographic coating mixture which required blending for 5-6 hours at minimum or overnight in some cases, can be finished in only 1-3 hours according to the present invention. Moreover, due to a brief blending of the photoconductive powder with the resin binder effectively suppressed at a lower level than in the conventional one-step dispersing process, realizing remarkable increase of photosensitivity of the resulting coating. Further, the solvents used for pre-treatment or wetting of the photoconductive powder need not be removed, but is compatible with many resin formulations since they can dissolve those various materials which are rather difficult to dissolve in many organic solvents.

The advantage of the invention lies in the fact that the resin formulations which employ polyisocyanate compounds as curing agent be used. Resins which can be cured by polyisocyanates and form electrophotographic coatings with excellent properties include alkyd resin, epoxy-ester resin, vinyl copolymers containing monomer ingredients selected from hydroxyethylacrylate, hydroxyethylmethacrylate, allyl alcohol, hydroxyethylacrylamide.

Another advantage of the present invention lies in the fact that an inorganic photoconductive powder with a rather large mean particle diameter having a high light sensitivity can be used in an electrophotographic coating. In the case of zinc oxide having a mean particle diameter greater than 1 micron it requires a relatively long grinding time with a resin binder and when it is dispersed until the mixture gives a smooth surface coating the coating exhibits a sensitivity substantially equal to that given by a coating containing zinc oxide of about 0.5 micron mean diameter. On the contrary, a coating containing the coarse zinc oxide can be obtained which exhibits a higher sensitivity than that containing the fine zinc oxide powder by the factor of 2 to even 4, when one resorts to a blending method such as by means of homogenizer for about 30 minutes.

Unfortunately, the coating thus prepared possesses an extremely rough surface which is hardly acceptable for practical applications.

By employing the method of the present invention, however, one can realize the high sensitivity as well as a sufficient degree of surface smoothness with the use of such coarse zinc oxide powder.

The following examples of procedures embodying the invention are given for illustrative purposes.

EXAMPLE I

100 parts by weight of photoconductive zinc oxide commercially available from Sakai Chemical Industries under the trade name "Tokugo" with a mean particle diameter of 1.98 microns as measures by the permeametry was charged and milled in a ball mill for together with 150

parts by weight of acetone as the pretreating liquid for about 1 hour. Then 16 parts by weight of styrenated alkyd resin varnish commercially available from Japan Reichhold Chemicals, Inc. under the trade name "Styresol 4400" and 11 parts by weight of polyisocyanate compound "Desmodur 1" from Bayer Chemische Werke (Germany) were added and the mixture was transferred into a homomixer which was driven for 5–10 minutes at 12,000 r.p.m.

The dispersion thus prepared was spread over the metallized surface of polyethyleneterephthalate film with vacuum coated aluminum layer (trade name "Metalmy" from Toyo Rayon Co.) to give a dry thickness of about 5–6 microns and dried. The drying was carried out at 50° C. for 16 hours so as to complete the curing of the binder.

The dried coating had a uniform surface with a smoothness similar to a coating from a mixture prepared by grinding in a ball mill jar the whole non-volatile ingredients with a suitable amount of solvent for the resin for 10 hours without the pretreatment of the zinc oxide.

For comparison, another coating was produced from a mixture prepared solely by blending with a homomixer or homoblender, also omitting the pretreatment; on the surface of the coating there was observed a number of agglomerates which were easily recognized by naked eyes, preventing it from practical utilities.

The sensitivity of each of these three coatings was measured in the following manner. After dark-adaptation over 2 days, a piece of the sample was negatively charged by corona discharge and the dark decay was measured.

Next, another piece was similarly charged and irradiated by light from an incandescent lamp to measure light decay property. The light decay curves were recorded with various illumination intensities which were adjusted by changing neutral density filters placed in front of the lamp. From the measured curves the following values were read.

V_t^L : the potential after irradiation at intensity I for a constant exposure time t sec.

V_o^L : the potential prior to the initiation of irradiation.

V_o^D : the initial potential at the measurement of the dark decay.

V_t^D : the potential after dark decay for t sec. and the residual potential ratio calculated by

$$\frac{V_t^L/V_o^L}{V_t^D/V_o^D} \times 100(\%)$$

for certain value of t was plotted on the ordinate, and the reciprocal logarithm of the exposure amount $I \times t$ on the abscissa. Thus the tone reproduction characteristic curve of the coating is obtained. The electrophotographic light sensitivity is defined as the value of $\log(1/I \times t)$ corresponding to the residual ratio of 35%.

In Table I are listed the important characteristics of the three coatings;

- prepared in accordance with the present invention,
- prepared by 10-hour ball milling without pretreatment, and
- prepared by blending with a homogenizer at 15,000 r.p.m. for 10 minutes.

V_o^D designates the initial potential, $V_{60}^D/V_o^D \times 100\%$ represents the dark decay characteristic, and the third column shows the decay of the potential when the charged sheet is wetted with purified Decalin with a voltmeter measuring probe thereon.

TABLE I

Preparation of coating mixture	V_o^D	V_{60}^D/V_o^D , air, percent	V_{60}^D/V_o^D , Decalin, percent	Sensitivity -log (It) 35%	Surface smoothness
(a) according to the invention, Example I.....	-200 V	94	90	-1.68	Good.
(b) 10 hour ball milling.....	-180	91	86	-2.18	Do.
(c) 10 minutes blending with homogenizer.....	-210	95	88	-1.65	Extremely rough.

The data in the table shows that the coating (a) has a higher sensitivity than (b) has with the difference of about 0.5 on log scale. Although the coating (c) exhibits the fastest light speed, it has a quite rough surface. Therefore, only the coating (a) has realized a high sensitivity inherent to the zinc oxide involved not at the expense of other properties such as surface smoothness.

EXAMPLE II

In this example, the same operations were repeated as in Example I except that the spectral sensitizers comprising 0.02 part by weight of brilliant blue FCF (Color Index No. 42090), 0.04 part by weight of eosine, and 0.05 part by weight of fluorescein were used which were added prior to pretreatment.

For comparison another coating obtained from a mixture prepared by 10-hour ball mill grinding of the zinc oxide and the resin binder eliminating the pretreatment. The two coatings are compared as for their sensitivities in Table II, which disclose that the former coating is higher in sensitivity than the latter by a factor of more than 4.

TABLE II

	Sensitivity
(d) Prepared in accordance with the invention, spectrally sensitized	-0.25
(e) Prepared by 10 hour ball milling, spectrally sensitized	-0.90

EXAMPLE III

100 parts by weight of rutile type titanium dioxide commercially available from Ishihara Sangyo Kaisha under the trade name R-840 and 150 parts by weight of methylethylketone as pretreating liquid were charged in ball mill jar and ground for 1 hour and a half. The mixture obtained was moved together with 40 parts of vinyl-chloride/vinyl acetate copolymer varnish (45% solid) to a homomixer which was rotated at 12,000 r.p.m. for 5–10 minutes. The resulting dispersion was coated to form an electrophotographic coating by the same procedures as were described in Example I.

The sensitivity of the coating was compared with that of another coating prepared by 15 hours ball milling in the conventional manner. Table III shows a sensitivity increase by the factor of 2 by making use of the invention.

TABLE III

	Sensitivity
(f) Prepared according to the invention	-3.30
(g) Prepared in a conventional manner	-3.62

EXAMPLE IV

This example differed from Example II only in that the formulation for the resin binder was changed to the following:

Vinyl copolymer comprising 34% of styrene, 51% of n-butylmethacrylate, and 15% of hydroxyethylmethacrylate; 12 parts by weight

Acrylated alkyd resin—3 parts by weight
Polyisocyanate (Takenate D102: from Takeda Chemical Industries)—7 parts by weight

A similar satisfactory result was obtained.

What is claimed is:

1. A method forming an electrophotographic coating by homogeneously dispersing a finely-divided inorganic photoconductor in an insulating film-forming binder select-

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ed from the group consisting of epoxyester resin cured by polyisocyanate and alkyd resin cured by polyisocyanate, and coating the resulting dispersion on a conductive substrate, characterized by that prior to the blending of the photoconductive powder with the insulating film-forming resin binder the photoconductive powder is blended with an organic solvent which is free of hydroxyl groups and carboxyl groups in its molecular structure, has a dielectric constant not lower than 10 at 20° C. and can dissolve said film-forming resin binder.

2. A method as claimed in claim 1 wherein said organic solvent is cyclohexanone.

3. A method as claimed in claim 1 wherein said inorganic photoconductive is zinc oxide.

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NORMAN G. TORCHIN, Primary Examiner

J. R. MILLER, Assistant Examiner

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