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[54] ELECTROSTATIC POWER COATING METHOD COMBINED WITH AN ELECTROPHOTOGRAPHIC PROCESS

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[52] **U.S. Cl.** .... **96/1 SD,** 96/1 R, 117/17.5
[51] **Int. Cl.** **G03g 13/08**
[58] **Field of Search** .... 96/1 R, 1 SD, 1.4; 117/17.5

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[57] ABSTRACT

An electrostatic powder coating method comprising; exposing a charged photoconductive toner layer formed on an electrically conductive substrate to an optical image; selectively removing the irradiation discharged toner particles from said toner layer at irradiated areas to form a toner image corresponding to said optical image; and then, while the remaining charged toner layer still retains a sufficient amount of charge, electrostatically spraying a second powder having the same charge polarity as that of said toner layer over the toner image bearing surface, whereby said second powder is preferentially deposited on the irradiated areas of said image bearing surface, is disclosed.

8 Claims, No Drawings

ELECTROSTATIC POWER COATING METHOD COMBINED WITH AN ELECTROPHOTOGRAPHIC PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrostatic powder coating method combined with an electrophotographic marking process utilizing a photoconductive toner. The present invention further relates to a method carried out on a plate bearing a photoconductive toner image thereon formed electrophotographically whereby a powder paint deposits selectively on the toner-deficient region of the marked plate to obtain a reversal paint powder distribution relative to the first toner image.

2. Description of the Prior Art

Electrostatic powder coating comprises, depositing a powder paint electrostatically charged with a negative or a positive polarity onto a grounded conductive material to be coated by an electrostatic attraction between the material and the charged powder paint, and then converting the deposited powder layer into a continuous one by thermal fusing or other suitable means.

On the other hand, an electrophotographic marking process is based on the electrostatic attraction between a photoconductive toner containing photoconductive ZnO and the material to be marked.

SUMMARY OF THE INVENTION

The present invention has been accomplished by recognizing the similarity of these two methods and is based on the electrostatic repulsion between the image-forming photoconductive toner which retains a sufficient amount of charge and a subsequently applied powder paint which is charged in the same polarity as the toner to cause a differential deposition of the powder paint on the toner-defficient region of the marked plate.

In the following description given hereinafter, the present invention will be explained more in detail; 1. First, a uniform layer of a photoconductive toner charged, for example, negatively is formed on a rust-removed steel plate or on a surface having a suitable electric conductivity. 2. An image of light and shadow to be reproduced is projected on the charged toner layer using an optical enlarger whereby the surface potential is markedly reduced at the light-struck areas of the charged toner layer where the attraction between the photoconductive toner and the plate substantially disappears. Since the remaining areas retain their surface potential, an electrostatic latent image is formed in the toner layer. 3. The photoconductive toner which has lost its charge is removed using an air stream, whereby a toner image appears on the plate. 4. Then an electrostatic powder coating is applied on the toner image bearing plate thus prepared using an electrostatically charged powder paint having the same polarity as that of the image-forming toner particles, whereby the powder paint particles deposit selectively on the toner-deficient regions of the plate as a result of coulomb repulsion affected on the paint particles by the toner particles present on the plate. The powder paint deposits on almost the entire surface of the plate except on the image areas which in general occupy only a slight portion of the entire area.

DETAILED DESCRIPTION OF THE INVENTION

The four procedural steps constitute the present invention. Additional embodiments which can be valuable from a practical standpoint can be carried out as follows. 5. When the plate thus coated is subjected to uniform exposure to light, the photoconductive toner loses its electrostatic charge completely, while the paint powder which is highly insulating and does not respond to light retains its charge. 6. Therefore, an air stream or a slight mechanical vibration can remove the discharged toner from the plate surface, thus providing a powder paint coating which carries an information containing image comprising the powder deficient region. 7. The powder paint coating may be fused by baking to form a continuous final coating layer or may be fused by the application of solvent or fixed by the application of a lacquer solution.

As will be clear from the above descriptions, the present invention enables an improved powder spray containg to form an information containing image therein with less labor.

Further explanation will be given for each procedural step and the materials included in the present invention.

a. Photoconductive toner

The desirable toner should retain in darkness a high electrostatic potential over a long period of time, as long as one to several tens of minutes and rapidly lose its potential when irradiated. The specifications of British Pat. Nos. 1,183,762 corresponding to U.S. Ser. No. 197,532 filed Nov. 10, 1971, now U.S. Pat. No. 3,775,103, which is in turn a continuation-in-part application of U.S. Ser. No. 615,384 filed Feb. 13, 1967, now abandoned and 1,210,071 corresponding to U.S. Pat. No. 3,607,368, French Pat. No. 1,536,725 corresponding to U.S. Ser. No. 115,764 filed Feb. 16, 1971, now abandoned in favor of continuation application Ser. No. 330,115, filed Feb. 6, 1973 and a continuation-in-part of U.S. Ser. No. 667,089 filed Sept. 2, 1967, now abandoned, and Japanese Patent Publication No. 12385/1969 disclose preferred structures and formulations for photoconductive toners. Generally speaking, a desirable performance can be obtained when the toner is constructed so as to pass therethrough a sufficient amount of active light, which can cause the photoconduction of the photoconductive ingredient of the toner, i.e., light which renders the photoconductor photoconductive. A typical example of such a structure is a transparent resinous core covered with a thin photoconductive surface coating. Toners having different structures may also be used in the present invention provided they have a sufficient level of photoconductivity. A commercially available product is EPM Photoner No. 327, made by the Fugi Photo Film Co., Ltd.

Usually, the size of toner ranges from about 20 to 150 microns.

b. Substrate (the material on which the photoconductive toner layer is formed)

Any substrate may be used for the present process provided that it has a suitable surface electrical conductivity value and that it does not exhibit an adhesive or a tacky nature against finely-divided powder. A preferred range of conductivity is not less than 10^{-10} (ohm square)$^{-1}$. Typical materials include metallic plates, paper or paint coated steel plates which have been treated with electrically conductive materials.

c. Formation of the photoconductive toner layer

Although a uniform photoconductive toner layer can be formed using a sieve, one may preferably resort to a specially designed toner dusting apparatus such as that described in Japanese Patent Publication No. 8838/1970 which can impart an electrostatic charge to the photoconductive toner simultaneously with the dusting operation.

The dusting layer should have a uniform dusting density over the entire area. The relationship between the dusting density and the electrophotographic characteristics is described in Applied Optics Supplement 3: p.124–128 (1969). The photoconductive toner dealt with in this report has particle sizes ranging from about 30 to 100 microns, and a density of 1.5. A preferred range of dusting density is about 50 to 150 g/m^2.

d. Charging

The charging of the photoconductive toner can be carried out simultaneously with the dusting or as a separate operation using corona discharge after dusting. The initial potential is higher with the former method than with the latter and at the same time the other properties are improved with the former method of charging.

e. Image exposure

Although image exposure is usually effected by projection of the image, contact exposure may also be employed provided that the nature of the original image is appropriate.

f. Development

Development is the removal of the photoconductive toner present at the light-struck areas after image exposure. Such differential removal can be effected by applying an air stream, vibrating the substrate or by combining these two operations. An example of developing apparatus can be found in the above-cited literature.

g. Powder paint

In this specification the term "powder paint" is used for convenience mainly to avoid confusion with the photoconductive toner, and is intended to cover an insulating powder which is to be applied on the toner image formed by the procedures up to 3. The necessary requirements for the powder paint are an insulating nature which is sufficient to retain an electrostatic charge thereon for a pre-determined period, and non-photoconductivity when irradiated with active light to the photoconductive toner used.

From a practical standpoint, most of the commercially available powder paints exhibit substantially no photoconduction at all, however, those with a very slight photoconductive response, which is negligible in comparison with that of the photoconductive toner used, may also be used. In brief, this requirement is significant to perform the step 5 smoothly.

Powder paints are commercially available. They comprise pigments dispersed in resinous materials which melt at a suitable temperature range to form continuous films, and usually have particle sizes of about 20 to 150 microns. Suitable resinous materials include epoxides, polyamides, polyesters, polyvinylchlorides, cellulose acetobutyrate, polyacrylate, etc.

Following literature references deal with powder paint technology; A. B. Zimmerman, G. Kappas, *Paint and Varnish Production*, 55 (2), p57 (1965), K. M. Oesterle, I. Szasz, *Journal of the Oil and Color Chemists Association*, 48 (10), p956 (1965), *Shell Chemical Paint Technology News* No. 69, T. Kubota, *Coating Technology* 67 (14), p8 (1962), British Pat. No. 1,040,897, and *Powder Coating and Fluidized Bed Techniques*, M. W. Ranney Noyes Data Co., 1971.

In addition to powder paints, insulating resin powders may also be used. Powders of suitable formulations meeting the requirements necessary may be suitably selected to form a reversal pattern with respect to the first formed photoconductive toner image.

h. Electrostatic coating of the powder paint

A powder paint is coated using an electrostatic spray coater, by using an electrostatic fluidizing bed impregnation, or by any other suitable means which are well known in the art. These techniques are so well known that no further explanation is necessary to one skilled in the paint arts in view of the numerous literature references published. The coating weight differs depending on the function, however, from an economical point of view, it may preferably be as high as possible provided that the powder paint will not deposit excessively on the toner image area. When a sufficiently contrasted toner image has been obtained, a powder paint coating of about a 50 to 100 micron thickness generally will result. To prepare a thick paint coating, the charge retaining capability of the photoconductive toner plays a very important role. To increase the repulsive potential of the photoconductive toner image, one may employ, for example, an additional charging of the image bearing material using a corona discharge immediately prior to the electrostatic coating.

i. Subsequent procedures

The subsequent procedures are all technically simple; uniform exposure may be carried out to discharge substantially the entire charge of the photoconductive toner. Generally speaking, powder paints or other insulating powders can retain an electrostatic charge thereon for about several hours, therefore, the charge attenuation on the powder paint can be ignored.

The removal of the photoconductive toner may be done according to the method described in paragraph f) above. Where perfect removal is required, an intense air flow may be employed which will, however, also blow off the powder paint to some extent. On the contrary, when uniformity and a high coating weight of the powder paint is of significance, an imperfect removal may be allowed.

Although the present invention discloses a new image-forming process per se, it can be used as a particularly advantageous method of precessing steel plate or other structural materials, for example, in ship building. A steel plate immediately after shot-blasting is subjected to the powder-paint coating according to the present invention. The photoconductive toner image is first formed to designate where welding or flame-cutting should be carried out subsequently. When the entire procedures of the present method are complete, those areas remain uncoated. The plate is treated using radio-frequency induction heating or other means to convert the powder paint layer into a firm continuous layer. On the coated plate thus processed, welding or flame-cutting operations are smoothly conducted at the naked areas avoiding the difficulties which would be accompanied with the existence of paint coating such as conventional shop primer at the areas to be welded or cut. Moreover, since the remaining solid areas are protected by the firm powder paint coating of 50 to 100 microns thick which has a far better rust-preventive property and durability than conventional shop-primer coatings. The overcoating need not be repeated after the building up of the materials, which reduces the number of coating operations surprisingly. Of the commercially available powder paints, there are those which have good adhesion to metallic materials such as steel plates. These parts, therefore, do not need any subcoating or primer-coating, which is quite desirable for the present invention since electrophotographic marking is carried out most advantageously on highly conductive substrates. Such powder paints include polyester and epoxides resin types.

The present invention has quite a unique feature when considered as an image recording technique, since the photoconductive material is not consumed at all where practiced under ideal conditions. This permits the use of a very expensive photoconductive material as long as it satisfies the necessary conditions required.

Processes based on similar principles and which can convert a negative into positive image or vise versa are disclosed in Japanese Patent Publication No. 19535/1964, U.S. Pat. Nos. 3,038,799 and 2,914,403. However, these processes are clearly different from the present invention in that they employ photoconductive layers which cannot be utilized repeatedly.

In particular, the processes described in the latter two patents comprise development with an electrically conductive toner of an electrostatic latent image formed on a photoconductive layer, and corona charging the toner-image bearing surface in darkness followed by a second development which gives rise to a reversal image. Such processes are known to be unable to provide a high quality final image mainly due to the fact that the corona ions are deflected by the conductive toner image, leaving a undesirable low surface charge density area around and contiguous to the conductive toner image area to cause a very unclear reversal image.

In the following, some specific examples will be given for a better understanding of the invention. These examples are not, however, to be interpreted as limiting.

Example 1

The following ingredients were blended in a ball mill jar.

Photoconductive Zinc Oxide	150 parts by weight
Silicone Resin Varnish (methyl phenyl polysiloxane a product of Fuji Kobunshi Kogyo K.K.)	40 parts by weight
Cyclohexane	100 parts by weight

The resulting mixture, 20 parts by weight, was added to 70 parts by weight of a polymethylmethacrylate powder having an average particle size of 70 microns. This mixture was then dried under stirring. A coated powder resulted. The polymethylmethacrylate powder had an extinction coefficient of 2.5 mm^{-1} for a 3800 A. wavelength light which corresponds to the intrinsic photoresponse region of ZnO.

This powder was sprinkled on an aluminum plate at a density of 80 g/m^2, and then the powder layer was exposed to a negative corona discharge. A surface potential of −395 volts was obtained. The powder layer was exposed to an optically positive line image by projection and then scanned by air spraying from a nozzle. Due to the air stream the powder remained only at the unexposed regions to form a reproduction of the original image. Still in darkness a commercially available red powder paint (a polyamide resin type) was sprayed over the image-bearing plate using an electrostatic powder sprayer manufactured by the GEMA Co. with a charging voltage of −6000 volts and an air pressure of 3.0 kgs/cm^2. The red powder deposited selectively on the background of the first image and a white image comprising the photoconductive toner was legible after paint coating. A fixing by lacquer coating could be effected on the plate thus prepared. Alternatively, the plate was uniformly illuminated to discharge the charge remaining on the first obtained image, and then subjected to an air stream, which completely removed the toner forming the first image. The plate was then heated to 230°C for 30 minutes whereby the red powder paint melted to form a continuous layer.

EXAMPLE 2

The following ingredients were blended in a ball mill jar for 20 hours.

Cadmium Yellow Orange	150 parts by weight
Epikote Ester Varnish (a trademark of the Shell Chemical Company, an epoxyester of dehydrated castor oil fatty acid with 40% oil length and non-volatile content of 50%)	48 parts by weight
Silicone Resin Varnish KR-211 (methyl phenyl polysiloxane a product of the Shin-etsu Chemical Inc., Ltd.)	23 parts by weight
Toluol	60 parts by weight

Glass beads were used as a core material which had a minimum size of 40 microns and the maximum size of 117 microns and a extinction coefficient of 1.0mm^{-1} for a 5500A. wavelength light corresponding to the intrinsic absorption region of Cadmium Yellow Orange. To 200 g. of the glass beads was added 80 g. of the blend. The mixture was dried under stirring followed by pulverizing in a mortar.

As a support, an art paper treated with colloidal alumina (coating weight on dry base was 2g/m^2) was used. The treated surface had a low surface resistance as well as a low tackiness.

On a sheet of this paper was sprinkled the above described photoconductive powder at the density of 60 g/m^2. The powder coating was charged negatively in the dark, exposed with an optically projected negative image, and air sprayed to form a first negative image. This image was then again charged using a negative corona; over this image was sprayed a negatively charged, finely-divided, nigrosine dyed polystyrene (particle size about 30 to 70 microns) whereby the polystyrene particles deposited only at the toner-deficient regions due to the electrostatic repulsion from the photoconductive toner. With subsequent uniform exposure and air spraying, the photoconductive toner particles were removed leaving a positive image comprising the polystyrene which was fused by the application of methylene chloride vapor.

Example 3

A sand blasted mild steel plate of a 400 mm × 1000 mm × 10 mm dimension was treated according to the process of the present invention, i.e., first marked electrophotographically and then subjected to an electrostatic powder coating.

The experimental specifications were as follows.

A. Electrophotographic marking:
- Photoconductive toner; EPM Photoner No. 327. A product of the Fuji Photo Film Co.
- Corona charging of photoner; −9000 volts.
- Dusting density of photoner; 90 g/m^2.
- Amount of exposure; 240 lux/secs.
- Air flow velocity of air-knife developer; 22m/sec.
- Initial potential of photoner layer; −300 volts.
- Remaining potential of photoner layer at the image areas after exposure; −280 volts.

B. Electrostatic powder coating.
- Powder paint; Epoxide powder paint.*
- Nozzle voltage; −6000 volts.
- Air pressure; 3.5 kg/cm^2.
- Coating Gun; GEMA Co. Electrostatic powder coater.
- Baking condition; 230°C, 30 minutes.
- Coating thickness; 60 microns.

* This Epoxide resin powder paint was prepared using the following procedure:

A mixture of following formulation was prepared by melt blending in a Z-shaped blade mixer at 80° to 90°C for 10 minutes.

Epikote 1004	(product of the Shell Chemical Co.)	68.48	pts by wt
Epicure 108	do.	11.52	do.
Flow Controlling Agent		1.00	do.
Pigment and Filler		19.00	do.

The melt was quickly cooled before the curing reaction proceeded too far. The cooled block was pulverized to particles of about 20 to 90 micron size.

The plate thus coated and having paint-uncoated marked lines was subjected to gas-flame cutting at the following conditions at the marked lines and a very satisfactory result, comparable to that for uncoated materials was obtained. Gas-flame cutter; Automatic gas-flame cutter of the Japan Flame Cutting Machines Ltd.

Type IK 12–E.

- Burner nozzle; No. 1
- Burner height; 5 cm.
- Oxygen pressure; Cutting, 2.5 kg/cm^2. Pre-heating, 0.3 kg/cm^2.
- Acetylene pressure; 0.27 kg/cm^2.
- Burner angle; 90°

The results obtained are shown as follows:

Treatment of the Test Plate	Coated According to the Invention	Uncoated	Epoxy-Zinc Rich Primer Coated
Cutting Velocity (mm/minute)	630	650	460
Smoothness of the cut plane	grade 1*	grade 1*	grade 3*

*Based on Welding Engineering Standard (WES) established by the Japan Welding Association.

Example 4

This same procedures as described in Example 3 were followed except that the photoconductive toner described in Example 2 was used. Similarly good results were obtained.

While the invention has been described in detail and in terms of specific embodiments thereof, it will be apparent to one skilled in the art that various modifications and changes can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. An electrostatic powder coating method comprising:

exposing a charged photoconductive toner layer formed on an electrically conductive substrate having a range of conductivity not less than 10^{-10}(ohm square)$^{-1}$ to an optical image; selectively removing the irradiation discharged toner particles from said toner layer at the irradiated areas to form a toner image corresponding to said optical image; then, while the remaining charged toner layer still retains a sufficient amount of charge, electrostatically spraying a second electrically insulating powder having the same electrostatic charge polarity as that of said toner layer over the toner image bearing surface, said second powder retaining its charge when irradiated by light which can dissipate the charge in said photoconductive toner, whereby said second powder is preferentially deposited on the irradiated areas of said image bearing surface; discharging the charged toner particles of said charged toner layer by uniform irradiation; and removing said discharged toner particles from said substrate.

2. The method as described in claim **1**, wherein said photoconductive toner layer contains photoconductive zinc oxide.

3. The method as described in claim **1**, wherein said second powder is a powder paint comprising a pigment in a resinous material selected from the group consisting of an epoxide resin, a polyamide resin, a polyester resin, a polyvinylchloride resin, and a cellulose acetate butyrate.

4. The method as described in claim **1**, wherein said method additionally comprises fusing the particles of said second powder.

5. The method as described in claim **1**, wherein said second powder is a powder paint comprising a resinous material selected from the group consisting of an epoxide resin, a polyamide resin, a polyester resin, a polyvinylchloride resin and cellulose acetate butyrate.

6. The method as described in claim **1**, wherein said removal of said irradiated discharged toner particles is by air blowing or by vibrating.

7. The method as described in claim 1, wherein said substrate is an uncoated metal plate and said second powder is a powder paint comprising a polyester or an epoxide resin.

8. A method of improving the smoothness of the cuts in a flame-cut metal pattern which comprises exposing a charged photoconductive toner layer formed on an electrically conductive substrate having a range of conductivity not less than 10^{-10}(ohm square)$^{-1}$ to an optical image; selectively removing the irradiation discharged toner particles from said toner layer at irradiated areas to form a toner image corresponding to said optical image; and then, while the remaining charged toner layer still retains a sufficient amount of charge, electrostatically spraying a second electrically insulating powder having the same electrostatic charge polarity as that of said toner layer over the toner image bearing surface, said second powder retaining its charge when irradiated by light which can dissipate the charge in said photoconductive toner, whereby said second powder is preferentially deposited on the irradiated areas of said image bearing surface; discharging the charged toner particles of said charged toner layer by uniform irradiation; removing said discharged toner particles from said substrate and flame cutting said substrate along the image areas formed by the removal of said discharged toner particles from said substrate.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,833,365 Dated September 3, 1974

Inventor(s) Kunio Hiwano et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE HEADING:

Under Assignees: add--Chugoku Marine Paints, Ltd. of Hiroshima, Japan--

Signed and sealed this 11th day of February 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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