United States Patent Office

3,169,062
Patented Feb. 9, 1965

3,169,062
ELECTROPHOTOGRAPHIC REPRODUCTION PROCESS

Kurt Walter Klupfel, Wiesbaden-Biebrich, Germany, assignor, by mesne assignments, to Azoplate Corporation, Murray Hill, N.J.

No Drawing. Filed Mar. 21, 1962, Ser. No. 181,433
Claims priority, application Germany Mar. 23, 1961
10 Claims. (Cl. 96—1)

In copending application Serial No. 150,458, filed November 6, 1961, there is described an electrophotographic reproduction process in which a latent resistance image is produced by the imagewise exposure to light of photoelectrically conductive but non-electrostatically charged insulator layer consisting of or containing organic photosemiconductors, a photoelectrically conductive but non-electrostatically charged insulator layer on a supporting material is placed on this latent resistance image, the whole is electrostatically charged from the supporting material side and the latent electrostatic image produced on the photoelectrically conductive coating of the superposed supporting material is made visible by known methods of electrophotography and may then be fixed, whereupon a mirror image of the latent resistance image is formed.

In this process, it is also possible for a supporting material to be used which is covered on both sides with the photoelectrically conductive insulator coating and the whole is then electrostatically charged from the supporting material side. The latent electrostatic image, produced on the coating remote from the latent resistance image to be reproduced, is made visible by the aforementioned methods and, where necessary, fixed, a non-reversed image of the latent resistance image thus being formed.

The present invention relates to an electrophotographic reproduction process in which a latent resistance image is produced by imagewise exposure of a photoelectrically conductive but non-electrostatically charged insulator layer consisting of or containing inorganic photosemiconductors, a photoelectrically conductive but non-electrostatically charged insulator layer on a supporting material is placed on this latent resistance image, the whole is electrostatically charged from the supporting material side and the latent electrostatic image produced on the photoelectrically conductive coating of the superposed supporting material is made visible by known methods of electrophotography and may then be fixed, whereupon a mirror image of the latent resistance image is formed. In this process too, it is possible for a supporting material to be used which is covered on both sides with the photoelectrically conductive insulator layer, the whole electrostatically charged from the supporting material side and the latent electrostatic image, produced on the layer remote from the latent resistance image which is to be reproduced, made visible by the aforementioned methods and where necessary fixed, whereupon a non-reversed image of the latent resistance image is formed.

The photoconductive coatings for the production of latent images are inorganic photoconductive substances, e.g., the oxides, sulfides, selenides, tellurides and iodides of zinc, bismuth, molybdenum, lead, antimony and cadmium.

Also, mixtures of such photosemiconductors can be used.

For the preparation of the photoelectric material, the photoconductive compounds are advantageously dispersed in organic solvents such as benzene, acetone, methylene chloride, ethylene glycol monomethyl ether or other organic solvents in which they will disperse readily, or in

mixtures of such solvents. The supporting material is coated with these dispersions in the normal manner, by immersion, painting, roller application or by spraying. The material is then heated to remove the liquid components.

Further, it is advantageous in this process also for the photoconductive compounds to be used together with organic resins, such as are described in the copending application, supra.

The inorganic photoelectrically conductive compounds are applied to the supporting material, with or without the resins, in known manner, e.g., by painting, roller application, immersion or spraying. The coating is then dried, whereupon an even, photoelectrically conductive coating is formed.

Supports primarily suitable for the photoelectrically conductive coatings are, in particular, foils made of metal, e.g., aluminum, zinc and copper, cellulose products such as paper, paper foils laminated to metal, cellulose hydrate, and cellulose esters such as cellulose acetate and cellulose butyrate.

If paper is used as a supporting material, it is advisable for it to be pretreated to prevent the penetration of the coating solution, e.g., with a solution of methyl cellulose or polyvinyl alcohol in water or with a solution of an interpolymer of acrylic acid methyl ester and acrylonitrile in a mixture of acetone and methyl ethyl ketone or with solutions of polyamides in aqueous alcohols or with dispersions of such substances.

To increase the light sensitvity of the reproduction coatings in the visible range of the spectrum, sensitizers are added in small quantities, i.e., about 0.0001 to 0.5% by weight of the solid substance, both to the solutions containing the insulating resin and to the solutions of the photosemiconductor. Such sensitizers, which are primarily dyestuffs, are disclosed, for example, in Belgian Patent No. 558,078.

Fillers and pigments such as kaolin, titanium dioxide and barium sulfate may also be added to the coating solutions in quantities of up to 30% by weight.

For the production of non-reversed copies from the latent image, paper, textiles, metals such as aluminum, copper and iron, cellulose hydrate foils or plastic foils are used as supporting materials. These supporting materials are coated with a solution of insulating natural or synthetic resins such as polystyrene, polyisobutylene, chlorinated rubber, polyvinyl chloride, chlorinated polyvinyl chloride, polyvinyl carbazole, colophony, coumarone resins and inorganic photosemiconductors. The supports may be coated on both sides or on one side only.

With the process of the invention either mirror image or nonreversed positive or negative reproductions of excellent quality are successfully obtained.

The method for the preparation of photoelectric mirror image copies is described below:

Example I

60 parts by weight of a polymethacrylic acid methyl ester (Plexigum® M7553) are dissolved in 320 parts by weight of toluene. To this solution, a solution of 0.05 part by weight of Rhodamine B extra (Schultz, Farbstofftabellen, 7th edition, vol. 1 (1931), No. 864) in 30 parts by weight of methanol is first added, with stirring, and then 180 parts by weight of extra pure zinc oxide is dispersed in the solvent mixture with a high-speed agitator. The suspension thus obtained has a viscosity of 50–55 seconds, as measured in a 2 mm. Ford beaker. This suspension is mechanically coated upon paper. The thickness of the coating, here designated as coating 2, should be 6 to 8μ. After drying, the paper is exposed under a positive film master for 5 seconds to a 250 watt

photographic bulb at a distance of 40 cm. A paper coated with 8 parts by weight of chlorinated rubber in 100 parts by volume of benzene is then placed on the exposed coating with its coating, here designated as coating *a*, on the image and the back is sprayed with negative charge, e.g., with a corona discharge. On the chlorinated rubber coating *a*, a larterally reversed, invisible electrostatic image of coating 2, consisting of positive charges, is first formed. The paper is now treated on the coated side thereof with a developer consisting of tiny glass balls and a very finely divided resin/carbon black mixture. As a result of friction against the glass balls, the resin/carbon black toner becomes positively charged; it is repelled from the positively charged image parts and settles on the uncharged parts. An image is formed which is laterally reversed negative with respect to the image on the coating 2 and a positive mirror image with respect to the original. It is slightly heated and thereby made durable (fixed); it shows good contrast. A number of copies can be prepared in this way from the exposed photoelectrically conductive insulator coating 2.

Similarly, it is possible for a visible image to be prepared if coating 2, after being exposed and charged, is treated with the developer and then fixed.

Example II

300 parts by weight of toluene are added to a solution of 160 parts by weight of a methyl silicone resin (50% in toluene) and this solution is mixed, by stirring, with a second solution consisting of 40 parts by weight of methanol and 0.2 part by weight of Acid Violet 6 BN (Schultz, Farbstofftabellen, 7th edition, vol. 1, No. 831). Into this mixture 190 parts by weight of zinc sulfide, a product commercially available under the name Sachtolith, are stirred and then dispersed by repeated grinding in a colloid mill. Further procedure is as described in Example I. After drying, the paper is placed coated side down on a page of a book with printing on both sides and is then exposed for 5 seconds to a 100 watt filament lamp. The light thus passes through the paper. After the exposure a paper that has been coated on both sides with a solution of 8 parts by weight of polyvinyl carbazole in 100 parts by volume of toluene is placed on the exposed coating. The exterior polyvinyl carbazole coating is then negatively charged and the coating that has been facing the latent image is developed with a developer as described in Example I. A non-reversed image of the master is obtained.

Example III

95 parts by weight of cadmium sulfide are introduced into a solution of 80 parts by weight of methyl silicone resin (50% in toluene), 100 parts by weight of toluene and 25 parts by weight of methanol and the mixture is homogenized by means of a high-speed agitator. This suspension is coated upon a transparent paper the surface of which has been pretreated to prevent the penetration of organic solvents and the coated paper is dried. Further procedure is as described in Example I, a mirror image of a page of a book with printing on both sides being projected with a camera upon the cadmium sulfide coating.

For the preparation of a copy the procedure is as described in Example I.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. An electrophotographic reproduction process which comprises producing a latent resistance image in a first photoconductive insulator layer containing an inorganic photosemiconductor by exposure of the layer to a light image, then placing a supported second photoconductive insulator layer in surface contact with the first layer with the layers facing each other, electrostatically charging the second layer by applying an electrostatic charge to the support for the second layer on the side remote from the second layer and developing at least one of the latent electrostatic images produced.

2. An electrophotographic reproduction process according to claim 1 in which the support for the second layer has a photoelectrically conductive insulator layer on only one side thereof.

3. An electrophotographic reproduction process according to claim 1 in which the support for the second layer has a photoelectrically conductive insulator layer on both sides thereof.

4. An electrophotographic reproduction process according to claim 3 in which the latent electrostatic image on the layer on the side of the support remote from the second layer is developed.

5. An electrophotographic reproduction process according to claim 1 in which the first layer is on a support.

6. An electrophotographic process according to claim 1 in which the second photoelectrically conductive insulator layer comprises an organic photosemicondutor.

7. An electrophotographic reproduction process according to claim 1 in which the second photoelectrically conductive insulator layer comprises an inorganic photosemiconductor.

8. An electrophotographic reproduction process according to claim 1 in which the photoelectrically conductive insulator layers include a resin.

9. An electrophotographic reproduction process according to claim 1 in which photoelectrically conductive insulator layers include a sensitizer.

10. An electrophotographic reproduction process according to claim 1 in which the photoelectrically conductive insulator layers include a filler.

References Cited in the file of this patent

UNITED STATES PATENTS

2,817,277	Bogdonoff	Dec. 24, 1957
2,825,814	Walkup	Mar. 4, 1958
2,833,930	Walkup	May 6, 1958
3,011,918	Silvernail et al.	Dec. 5, 1961
3,051,569	Sugarman et al.	Aug. 28, 1962
3,057,719	Byrne et al.	Oct. 9, 1962
3,084,061	Hall	Apr. 2, 1963

FOREIGN PATENTS

168,181	Australia	Dec. 7, 1956