

1

3,072,479

ELECTROPHOTOGRAPHIC PLATES COMPRISING SOLID SOLUTIONS OF OXAZOLONES

Günther Bethe, Karlsruhe, Germany, assignor, by mesne assignments, to Azoplate Corporation, Murray Hill, N.J., a corporation of New Jersey
No Drawing. Filed May 29, 1957, Ser. No. 662,320
24 Claims. (Cl. 96—1)

This invention relates to photographic reproduction and more particularly to electrophotographic processes, namely processes in which an electrostatic latent image is produced by utilizing the photoconductive property of certain substances (i.e. whose electrostatic conductivity varies dependent on the intensity of illumination). The electrostatic latent image may be produced in a conventional exposure operation, for example by means of a lens-projected image or by contact-printing techniques, whereby a non-visible electrostatic charge pattern (the so-called electrostatic latent image) is created on the charged surface of a suitable material; in such pattern the charge density at any point is related to the intensity of illumination obtaining at that point during the exposure. The latent image may be developed—i.e. rendered visible—by means of an electroscopic powder, such as a colored synthetic resin powder, and the resulting visible image may be fixed by rendering the powder permanently adherent to a surface on which the image is desired, for example, in suitable cases, by heating to fuse the powder particles to the surface.

In electrophotographic processes the electrostatic latent image is commonly formed on the surface of a photoconductive insulating layer carried on a support. For example, material comprising such support and photoconductive layer is sensitized by applying a uniform charge to the surface of the photoconductive layer, by means of a corona discharge, which charge is retained owing to the substantial insulating property, i.e. the low conductivity, of the layer in the dark. On exposure as described above, the photoconductive property of the layer causes the conductivity to increase in the illuminated areas to an extent dependent on the intensity of illumination, whereby the charge in the illuminated areas leaks away, leaving unaffected the charge located in the unilluminated areas, thus forming the aforementioned charge pattern or electrostatic latent image.

Electrophotographic processes are especially useful, for example, in connection with office duplicating, as they offer a wholly dry copying process. Much interest has been aroused and investigation made, particularly in respect to the natures of suitable materials comprising the support and the photoconductive insulating layer thereon, for use in such processes.

Photoconductive substances that have been employed for the purpose in question are, of the inorganics, primarily selenium, but also sulfur and cadmium sulfide, and of the organics, primarily aromatic hydrocarbons such as anthracene, naphthalene, benzidine, anthraquinone.

Various methods have been proposed also for forming or applying the photoconductive layer on the support. The relative desirabilities of these various methods, and of the various photoconductive substances which have hitherto been employed, depend on a number of factors, such as the light-absorption properties and the physical smoothness and homogeneity of the surface of the layer. It is found that a high absorption in the visible spectrum is advantageous while a smooth and homogeneous surface is desirable to prevent undesirable mechanical adhesion of developer powder to the surface, which impairs the definition of the image when developed.

Of the inorganic substances, selenium in particular gives

2

very homogeneous coatings with perfectly smooth surface, these being obtained by vacuum deposition of the vaporized selenium upon a conductive support. Selenium coatings produced in this manner have good light-absorption and their photoconductivity in the visible region of the spectrum is good. However, the preparation of coatings of this sort by vapor deposition is a lengthy and expensive process.

The organic substances hitherto proposed have either no absorption at all or only very slight absorption in the visible part of the spectrum. Moreover, they precipitate in crystalline form upon the conductive support and therefore produce coatings with rough and insufficiently homogeneous surface, such as those mentioned above as undesirable.

According to the present invention, there is provided a material for use in electrophotographic processes which is capable of being rendered light-sensitive by applying to its surface an overall electrostatic charge. The disadvantages arising from unevenness and lack of homogeneity of the photoconductive coating are completely overcome while at the same time, various advantages are provided.

The process of the present invention uses fluorescent photoconductive substances and consists in the preparation, using organic solvents, of solutions of organic substances that are both colored and fluorescent in admixture with certain resins. These solutions are applied to conductive supports and are characterized by the fact that after removal of the solvent there remain clear, optically homogeneous coatings in which no crystalline structure can be even radiographically detected; in this sense, they can be termed solid solutions.

In processes of the type described, anthracene has been proposed as a photoconductive substance and while anthracene is a fluorescent organic compound, it is colorless. Coatings made photoconductive by means of anthracene therefore require light rays of very short wave-length. Such coatings, moreover, are not suitable for the reproduction of colored originals. Certain fluorescent inorganic compounds such as cadmium sulfide in association with zinc sulfide have also been proposed.

In practicing the invention, the photoconductive substances may be fluorescent dyestuffs of the fluorescein or rhodamine type, and also certain substances having the chemical constitution of 2-aryl-4-arylidene-oxazolones, while the supports used may be, for example, aluminium or other electrically conductive plates or foils, paper, or plastic foils, of, for example, synthetic resins, regenerated cellulose or cellulose derivatives, or other materials conventionally used hitherto as supports for photoconductive layers in electrophotographic processes.

The invention further provides a method for preparing the above-described material which material comprises a support carrying a photoconductive layer. This method comprises applying to the support a layer of a solution of the resin and the photoconductive substance in an organic solvent, the amount of the resin in the solution, in proportion to the amount of the photoconductive substance, being such that, on removing the organic solvent from the applied layer, the photoconductive substance forms a solid solution with the resin.

Examples of the resins to be used in conjunction with the colored fluorescent organic substances include polystyrene and other polyvinyl resins capable of being used as individual polymers or in interpolymerization, synthetic maleic-acid resins, coumarone resins, indene resins and silicone resins. Natural resins, such as balsam resins, can also be used.

Organic solvents that may advantageously be used include benzene, acetone, methylene chloride and other

halogenated hydrocarbons, ethylene glycol monomethyl ether and other glycol-ethers and mixtures thereof.

The solution forming the photoconductive layer may be applied to the support by conventional coating methods, such as roller coating, spray coating or whirl coating. Alternatively, the photoconductive substance and the resin may be applied in the form of a melt.

The present invention enables completely homogeneous, transparent, photoconductive coatings with smooth surfaces to be produced, possessing good photoconductivity in the visible region of the spectrum and having good electrical insulation properties when unilluminated. Furthermore, the colored fluorescent organic substances can be selected for maximum response in any desired spectral region, whereby material can be produced for any particular light source the use of which is contemplated for the exposure operation of an electrophotographic process.

Not all organic substances that are both colored and fluorescent are equally suitable for the present invention. Those compounds which have sufficient photoconductivity to be used in the present process can be easily ascertained, e.g. by means of the following test:

After the photoconductive substance, with or without addition of a resin, has been coated, e.g. onto a metallic support, an electric charge is applied to the layer and the state of the charge is then measured by means of a high-quality electrostatic voltmeter without touching the layer or affecting the charge. The voltage drop during a certain period of exposure is an index of the light-sensitivity of the photoconductive substance. The photoconductive layer charged by corona discharge to 400 volts is exposed to an incandescent lamp of 100 watt at a distance of 30 cm. for one second: the voltage must drop to below 40 volts.

Alternatively, a practical test may be made by the production of an electrophotographic image on a prepared material.

The use of the photoconductive coatings provided by the invention confer advantages thought to be due to the mobility of the conductance electrons in the colored fluorescent substances and to the fact that in solid solutions fluorescence is retained. The conductance mechanism is presumably used upon the formation in the solid solution of conductivity chains of the fluorescent component, the configuration of which chains is dependent on the concentration of the colored fluorescent substance in the resin and on the nature of the resin itself.

This would also explain the phenomenon that the photoelectric efficiency of the coatings rises with the concentration of the colored fluorescent organic substance in the resin. Above a certain critical concentration, the colored fluorescent substance shows a tendency to crystallize out as the coating solidifies. However, it is in the vicinity of this so-called crystallization point that the photoelectric conductivity is greatest, and for this reason it is desirable that the concentration of the colored, fluorescent substance in the resin be substantially equal to that obtaining at the crystallization point. It has been found that the concentration of photoconductive substance to resin is preferably within the range 2:1 to 1:10.

Electrophotographic materials embodying the invention not only have outstanding homogeneity and high insulation property of the photoconductive coating as already mentioned, but also the further very important advantage of considerably lower attenuation of light affecting the photoconductive layer. If as support for the photoconductive layer a transparent or translucent support such as a suitable paper or plastic foil is used, the images produced by electrophotographic means can be used as intermediate originals in contact-copying processes. This has hitherto not been feasible owing to the nature of previously known photoconductive layers. Another advantage over known materials for electrophotographic processes is that the invention enables colored originals to be reproduced.

The following examples serve to illustrate the invention:

Example 1

A solution is prepared consisting of

- 1 g. of coumarone resin 701/70 (sold by Gesellschaft für Teerverwertung, Duisburg-Meiderich)
- 0.12 g. of "Fluorol" 5G, a dye made by condensing p-cresol with phthalic anhydride in sulfuric acid to dimethyl fluorane, then effecting ring closure in oleum, followed by reduction with Zn/NaoH
- 10 cc. of toluene

The solution appears yellowish-red by transmitted light. About 3 cc. of this solution is used to cover an aluminium plate of about 18 x 24 cm. or pro rata. After the solution has been uniformly distributed over the surface of the plate, the toluene is evaporated and a clear, transparent lacquer coating is obtained on the aluminium plate. To remove the last traces of toluene from the lacquer coating the plate is reheated to 50-60° C.

Example 2

A solution is prepared from

- 1.0 g. of polystyrene of a molecular weight corresponding with the K-Wert (K-value) 55
- 0.25 g. of "Fuorol" 5G
- 0.25 g. of "Fluorol Grüngold," a dye made by heating perylenedicarboxylic acid with PCl₅ in nitrobenzene, then condensing with isobutanol and PCl₅
- 17.0 cc. of trichloroethylene

The procedure described in Example 1 is repeated using 3 cc. of this solution for coating an aluminium plate of the same dimensions, or pro rata.

Example 3

1 g. of 2-phenyl-4-diphenylidene-oxazolone (melting point 183° C.) and 1 g. of an unsaponified ketone-aldehyde-condensation resin, e.g. a product manufactured by Chemische Werke Hüls Aktiengesellschaft, Marl, and sold under the registered trademark "Kunstharz AP," are dissolved in 30 cc. of benzene. About 15 cc. of this solution are evenly coated onto a paper foil of 28.8 cm. by 21.0 cm. (DIN A4). After evaporation of the solvent, a firmly adhering layer remains on the surface of the paper foil. After applying a positive electrostatic charge to the layer by means of a corona discharge and after exposure of the electrostatically charged layer to an original, either in a contact printing process or by means of diascopic or episcopic projection, the foil, which now bears a latent image of the original, is dusted with a black resin powder obtained by fusing 30 parts by weight of polystyrene (K-Wert 55), 30 parts by weight of a maleic acid resin modified with rosin sold under the registered trademark "Beckacite K 105," and 3 parts by weight of carbon black, and subsequently finely grinding the fused mass. The dusted foil is heated, whereupon an image of the original becomes visible against a light-yellow background.

Example 4

0.5 g. of 2-phenyl-4- α -naphthylidene-oxazolone (melting point 171° C.), 0.5 g. of 2-phenyl-4-p-dimethylaminobenzyldene-oxazolone (melting point 216° C.) and 1 g. of a maleic acid resin modified with rosin, e.g. a resin sold by the Reichhold Chemie AG. of Hamburg under the registered trademark "Beckacite K 105," are dissolved in 30 cc. of benzene. The solution is coated, for instance by means of a plate-whirler, onto an acetate foil and then dried.

In an electrophotographic process, such as the one described in Example 1, direct images with good contrasts are produced on the foil, which are clearly visible against a yellow background and may, e.g., be used as intermediate originals for making subsequent prints of the diazo-type process.

Example 5

1 g. of 2-phenyl-4-p-nitrobenzylidene-oxazolone (melting point 239° C.) and 2 g. of coumarone resin 701/70 sold by the Gesellschaft für Teerverwertung, Duisburg-Meiderich, are dissolved in a mixture consisting of 15 cc. of benzene and 15 cc. of dimethyl formamide. The solution thus obtained is then coated either onto a paper foil prepared in accordance with either one of the following U.S. Patents No. 2,534,650, No. 2,681,617, or No. 2,559,610, or onto an aluminium foil the surface of which had been made grease-free. After evaporation of the solvent, the coated layer adheres firmly to the surface of the foil.

In an electrophotographic process, images with good contrasts are produced on the coated foil, which are fixed by heating and then transformed into a printing plate by applying a 50% ethyl alcohol solution to the foil, rinsing with water and inking with greasy ink and 1% phosphoric acid. Positive printing plates are obtained which may be clamped into a printing apparatus and used for printing.

Example 6

Instead of the 2-phenyl-oxazolone compounds mentioned in Examples 3, 4 and 5, there may be used with equally good results the following 2-phenyl-oxazolone compounds:

- 2-phenyl-4-p-methoxybenzylidene-oxazolone (melting point 179–180° C.)
- 2-phenyl-4-p-hydroxy-benzylidene-oxazolone (melting point 158° C.)
- 2-phenyl-4-p-chloro-benzylidene-oxazolone (melting point 198° C.)
- 2-phenyl-4-m-chloro-benzylidene-oxazolone (melting point 159° C.)
- 2-phenyl-4-m-nitro-benzylidene-oxazolone (melting point 174° C.)
- 2-phenyl-4-o-nitro-benzylidene-oxazolone (melting point 166° C.)

The oxazolone compounds listed above are yellow, and most of them have already been described in the literature. They are obtained by causing equimolecular quantities of hippuric acid and an aromatic aldehyde, such as benzaldehyde, to react with each other. The basic products are dissolved in a mixture of glacial acetic acid and acetic acid anhydride, to which anhydrous sodium acetate has been added, and the solution is then heated for about half an hour to 80–90° C. in a steam bath. The oxazolone compound in question precipitates as a crystalline substance, which may subsequently be recrystallized from alcohol or benzene.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is, therefore, to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. An electrophotographic material comprising an electrically conductive support layer and a photoconductive insulating layer, the latter comprising a solid solution of a 2-aryl-4-arylidene-oxazolone in an insulating resin.

2. A photographic reproduction process which comprises exposing an electrostatically charged photoconductive insulating layer, supported on a conductive backing, to light under a master and developing the resulting image by treatment with an electroscopic material, the photoconductive layer comprising a solid solution of a 2-aryl-4-arylidene-oxazolone in an insulating resin.

3. An electrophotographic material according to claim 1 in which the concentration of the oxazolone in the resin is in the range about 2:1 to 1:10.

4. A photographic reproduction process according to claim 2 in which the concentration of the oxazolone in the resin is in the range of about 2:1 to 1:10.

5. An electrophotographic material according to claim 5

1 in which the oxazolone is 2-phenyl-4-p-chlorobenzylidene-oxazolone.

6. An electrophotographic material according to claim 1 in which the oxazolone is a 2-phenyl-4-p-nitrobenzylidene-oxazolone.

7. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-alphanaphthylidene-oxazolone.

8. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-diphenylidene-oxazolone.

9. A process according to claim 2 in which the oxazolone is 2-phenyl-4-diphenylidene-oxazolone.

10. A process according to claim 2 in which the oxazolone is 2-phenyl-4-naphthylidene-oxazolone.

11. A process according to claim 2 in which the oxazolone is 2-phenyl-4-p-dimethylamino-benzylidene-oxazolone.

12. A process according to claim 2 in which the oxazolone is 2-phenyl-4-p-nitrobenzylidene-oxazolone.

13. A process according to claim 2 in which the oxazolone is 2-phenyl-4-p-methoxybenzylidene-oxazolone.

14. A process according to claim 2 in which the oxazolone is 2-phenyl-4-p-hydroxy-benzylidene-oxazolone.

15. A process according to claim 2 in which the oxazolone is 2-phenyl-4-p-chloro-benzylidene-oxazolone.

16. A process according to claim 2 in which the oxazolone is 2-phenyl-4-m-chloro-benzylidene-oxazolone.

17. A process according to claim 2 in which the oxazolone is 2-phenyl-4-m-nitro-benzylidene-oxazolone.

18. A process according to claim 2 in which the oxazolone is 2-phenyl-4-o-nitro-benzylidene-oxazolone.

19. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-p-dimethylamino-benzylidene-oxazolone.

20. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-p-methoxybenzylidene-oxazolone.

21. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-p-hydroxy-benzylidene-oxazolone.

22. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-m-chloro-benzylidene-oxazolone.

23. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-m-nitro-benzylidene-oxazolone.

24. An electrophotographic material according to claim 1 in which the oxazolone is 2-phenyl-4-o-nitro-benzylidene-oxazolone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,296,589	Yule	Sept. 22, 1942
2,297,691	Carlson	Oct. 6, 1942
2,663,636	Middleton	Dec. 22, 1953
2,692,178	Grandadam	Oct. 19, 1954
2,766,233	Kartinos et al.	Oct. 15, 1957
2,809,954	Kazenas	Oct. 15, 1957
2,825,814	Walkup	Mar. 4, 1958
2,862,815	Sugarman	Dec. 2, 1958
2,954,291	Clark	Sept. 27, 1960

FOREIGN PATENTS

134,610	Australia	June 19, 1947
201,416	Australia	Apr. 13, 1956

OTHER REFERENCES

Lang: Handbook of Chemistry, 7th Ed., Handbook Pub. (1949), pages 1069 and 1073.

Winslow: Journal American Chemical Society, vol. 77, September 1955, pages 4751–4757.

Kallman et al.: Physical Review, March 15, 1955, pages 1596–1610.

(Other references on following page)

Deribere: Applications Pratiques de la Laminescence, Dunod (1938), pages 151-152.

Zchodro: J. Chim. Phys., vol. 29, pages 59-64 (1929).

Petrikaln: 2—Phys. Chem., vol. 10B, pages 9-21 (1930).

Vartanian: Acta Physicochimica U.R.S.S., vol. XXII, No. 2, pages 201-224 (1947).

Wainer: Phot. Eng., vol. 3, No. 1, 1952, pages 12-18.

Lewis et al.: Chemical Abstracts, vol. 36 (1942), col. 6081.

Laffitte et al.: Chemical Abstracts, vol. 48 (1954), col. 8651.

The Merck Index, 6th Ed., Merck and Co., pages 126, 82-83 and 825.