

[54] **PHOTOCONDUCTIVE REACTION
PRODUCT OF N -BETA- CHLORETHYL
CARBAZOLE AND FORMALDEHYDE**

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[58] Field of Search..... 96/1, 1 PC, 1.5;
260/67.5

[56] **References Cited**

UNITED STATES PATENTS

3,597,195	8/1971	Verhille et al.	96/1.5
3,526,502	9/1970	Murakami et al.	96/1.5
3,287,121	11/1966	Hoegl	96/1.5

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4,221,875 10/1967 Japan..... 96/1.5

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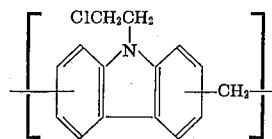
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[57] **ABSTRACT**

A xerographic plate including a resinous organic photoconductive composition obtained from the reaction between n-beta-chloroethyl carbazole and formaldehyde satisfying the formula:



and an electrophotographic process employing the same.

13 Claims, No Drawings

PHOTOCONDUCTIVE REACTION PRODUCT OF N-BETA-CHLORETHYL CARBAZOLE AND FORMALDEHYDE

BACKGROUND OF THE INVENTION

This invention relates to a photoconductive material and, more particularly, to the use of such a material in electrophotography.

The xerographic process as originally disclosed by Carlson in U.S. Pat. No. 2,297,691 generally involves applying a uniform electrostatic charge to a photoconductive insulating layer which makes up the surface of a xerographic plate so as to sensitize it. The plate is then exposed to an image of activating electromagnetic radiation such as light, X-ray, or the like, which selectively dissipates the charge in illuminated areas leaving behind charge in the non-illuminated areas to form a latent electrostatic image. The image so obtained is then developed or made visible by deposition of finely divided electroscopic marking material on the surface of the photoconductive insulating layer as a result of which the marking material conforms to the pattern of the latent image. Where the photoconductive insulating material is reusable, this visible image of finely divided or powdered marking material is then transferred to a second surface, such as a sheet of paper, and fixed in place thereon to form a permanent visible reproduction of the original. Where, on the other hand, a less expensive, non-reusable photoconductive insulating material is employed the toner particles may be fixed in place directly on its surface with the consequent elimination of the transfer step from the process.

In the earlier Carlson work coatings of anthracene, melted sulfur, and the like, were employed as the photoconductive insulating materials. However, these materials were found to have low sensitivity and produced only fair images at best under present standards. A great deal of development effort has been extended in attempting to provide improved photoconductive insulating layers for xerographic plates resulting in the production of a number of organic photoconductors such as, for example, polyvinyl anthracene; 2,5-bis-(p-amino phenol)-1,3,4-oxadiazole; polyvinyl carbazole and others. Another major area of xerographic plate development involves the binder plate in which finely divided photoconductive material such as, cadmium sulfide, cadmium selenide, zinc sulfide, antimony sulfide, mercuric oxide, lead iodide, lead sulfide, lead telluride, and other materials are dispersed in a film-forming insulating binder to make up the photoconductive insulating layer of a xerographic plate more fully described in U.S. Pat. No. 3,121,006 to Middleton and Reynolds. Although certain of these materials have been found to have a limited commercial utility, they suffer from various deficiencies such as low dark resistivity, poor sensitivity, high costs, poor mechanical properties and mainly from the fact that they are not reusable to make a rapid succession of images in the copying process. Accordingly, high quality xerographic plates made with photoconductors such as, elemental selenium and its alloys in the amorphous form, as described in U.S. Pat. No. 2,970,906 to Bixby have been found to be very successful from the commercial point of view because of the fact that they can be made in very smooth layers, they're reusable and can produce high resolution images and are fairly sensitive to visible light and X-ray radiation. Mechanically, this preferred xerographic

plate is fairly soft and eventually suffers surface degradation from abrasion with developing material after the production of 50,000 to 100,000 copies. In addition, the amorphous form of selenium is not as stable so that when plates including this type of selenium photoconductive layer are exposed to heat or certain solvent vapors they frequently are converted to inoperative crystalline forms of selenium. Though this preferred electrophotographic material suffers from these drawbacks, the amorphous selenium xerographic plate is the plate of preference in this field because other photoconductors such as the photoconductive aromatic polymers and binder plates described supra generally have low sensitivity, lack of reusability, relatively low abrasion resistance, rough surface characteristics and similar deficiencies. In addition, many of these materials can be sensitized only by negative and not by positive corona discharge techniques, that is, they are not ambipolar. Since negative corona discharge generates much more ozone than positive corona and since it is much more difficult to control negative corona discharge so as to uniformly charge the photoconductive layer, this also stands as a substantial drawback to the use of many of the alternatives to the amorphous selenium plate.

There has, therefore, been demonstrated a continuing need for electrophotographic materials having improved spectral response, sensitivity, reusability and mechanical properties.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a novel xerographic plate devoid of the above noted disadvantages.

Another object of this invention is to provide a reusable xerographic plate having spectral sensitivity that extends over a wide range.

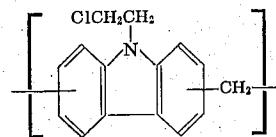
Still another object of this invention is to provide a reusable xerographic plate having high thermal stability and resistance to solvents.

Yet another object of this invention is to provide a xerographic plate which is resistant to abrasion and which is mechanically strong.

Yet another object of this invention is to provide a novel xerographic imaging process employing a xerographic plate with exceptionally good imaging properties.

Yet still a further object of this invention is to provide an electrophotographic plate having extremely high resolution imaging.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speaking, by providing a novel xerographic plate including a resinous organic photoconductive composition obtained from the reaction between n-beta-chloroethyl carbazole and formaldehyde satisfying the formula:



This organic photoconductive material is found to possess excellent xerographic properties when compared,

for example, to an n-ethylcarbazole-formaldehyde resin. Other conventionally available photoconductive materials unlike the compound of the instant invention even though having relatively low molecular weights with an intrinsic viscosity of 0.089 dl/g (measured in n-methyl-2-pyrrolidone at 30°C) are insoluble in toluene, dioxane, tetrahydrofuran, etc. and only soluble in polar solvents of high boiling points. They are, therefore, extremely difficult to apply on a support as a coating and, therefore, are not practical for employment in electrophotographic plates.

The organic photoconductive material of the present invention is synthesized by heating n-beta-chloroethyl carbazole the synthesis of which is well known and may be found, for example, in Nippon Kagaku Zasshi, Volume 85, 1964, page 880, and formaldehyde in the form of paraformaldehyde, formalin, or trioxane, etc. in an organic solvent, for example, dioxane or tetrahydrofuran in the presence of an acid catalyst. More specifically, 23 grams of n-beta-chloroethyl carbazole and 3 grams of paraformaldehyde are dissolved in 200 ml of dioxane and 1 gram of concentrated sulfuric acid is added to the resultant solution. The mixture thus obtained is heated at a temperature of 90°C for 4 hours with agitation and then poured into 3.1 liters of vigorously agitated methanol to obtain a white precipitate. The precipitate is separated by filtering and dissolved in 200 ml of tetrahydrofuran and the solution so obtained is poured into methanol to obtain a refined precipitate. The weight of the precipitate after drying is found to be 20.2 grams. The molecular weight of the resin obtained in this manner is found to be 14,000 by the vapor pressure repression method. The organic compound thus obtained is solution coated on a conducting support such as a metal sheet, paper sheet, or plastic film treated to impart conductivity to a thickness of up to 80 microns as a dry layer or preferably 2 to 20 microns. A suitable plasticizer may be employed to improve flexibility such as a chlorinated paraffin. The amount of the plasticizer added to the polymer may range from 0 to 100 weight percent based on the weight of the polymer. In addition, the light sensitivity may be improved by incorporating well known sensitizers. Excellent results have been obtained if the amount of the sensitizer added is less than 10 % by weight of the electrophotographic composition.

The electrophotographic layer so prepared if sufficiently dry is found to be substantially free from residual solvent and, therefore, capable of being uniformly charged in the dark by a corona discharge process, exposed to form a latent electrostatic image, and subsequently developed employing well known developing techniques such as, for example, cascade development or a liquid developing process. Where it is desirable to employ the cascade developing process, the developed image may be fixed by slightly heating the developed toner image or placing the toner image in the vapor of an organic solvent capable of dissolving the resin composition in the toner.

Any suitable coating technique for forming the photoconductive film of the present invention may be employed. Typical methods of coating include: flow coating, bar coating, dip coating and Mayer rod drawdown. It should be understood, however, that whatever method is employed to either coat or form the organic photoconductive materials into the photoconductive film of the present invention uniformity of thickness

and surface smoothness ought to be controlled so that they conform to those accepted electrophotographic standards well known in the art. The coating of the photoconductive material of the present invention should be uniformly deposited in thicknesses specified to a tolerance of plus or minus 25% and preferably to a tolerance of plus or minus 10% of nominal thickness. The surface smoothness of the photoconductive member of the present invention should be such that conventionally known particulate developers having particle sizes from about 2 to 10 microns can be readily removed therefrom.

Any highly insulative resinous film-forming binder may be employed in the system of the present invention to form the electrophotographic plate of the present invention. Typical insulating resin binders include: styrene/butadiene copolymers, polystyrenes, chlorinated rubbers, polyvinyl chlorides, vinyl chloride/vinyl acetate copolymers, polyvinylidene chloride, nitrocellulose, polyvinyl acetate, polyvinyl acetal, polyvinyl ether, silicone resins, methacrylic resins, acrylic resins, phenol resins, alkyd resins, and urea/aldehyde resins.

Any suitable electroconductive base may be employed in the system of the present invention. Typical such electroconductive bases include: metallic plates, fabricated of chromium, aluminum, brass, stainless steel, copper, zinc and alloys thereof; paper treated to acquire electroconductivity; and plastic films fabricated of aluminized Mylar (polyethyleneterephthalate) or conductive polymers.

Any suitable plasticizer may be employed in practicing the system of the present invention. Typical plasticizers include: chlorinated paraffin, phosphate plasticizers, phthalate plasticizers, and chlorinated biphenol, among others.

Any suitable sensitizer may be employed in practicing the system of the present invention. Typical sensitizers include: tetracyanoethylene, tetracyanoquinodimethane, chloranil, bromanil, alphanaphthalquinone, anthraquinone, methylene blue, crystal violet, and malachite green, among others.

Any suitable method of charging may be employed in practicing the system of the present invention. Typical methods of charging include: electric charging in a vacuum, corona charging, friction charging and induction charging more fully described in U.S. Pat. Nos. 2,934,649 and 2,833,930 respectively and roller charging more fully described in U.S. Pat. No. 2,934,650.

Any suitable method of exposure may be employed in practicing the system of the present invention. Typical methods of exposure include: reflex, contact, holographic techniques, non-lens slit scanning systems, and optical projection systems involving lens imaging of opaque-reflection subjects as well as transparent film originals.

Any suitable method of developing may be employed in practicing the system of the present invention. Typical methods of developing include: power cloud development more fully described in U.S. Pat. Nos. 2,725,305 and 2,918,910; cascade development more fully described in U.S. Pat. Nos. 2,618,551 and 2,618,552; and touchdown development.

Any suitable method of fixing the developed image obtained in practicing the system of the present invention may be employed. Typical methods of fixing include: heat-pressure fusing, radiant fusing, combina-

tion radiant, conductive and convection fusing, cold pressure fixing and flash fusing.

To further define the specifics of the present invention the following examples are intended to illustrate and not limit the particulars of the present invention. Parts and percentages are by weight unless otherwise specified.

EXAMPLE I

10 parts by weight of n-beta-chloroethyl carbazole-formaldehyde resin and 5 parts by weight of chlorinated paraffin are dissolved in 50 parts of toluene. The resultant combination is coated on an aluminum sheet to a thickness of 5 microns as a dry layer and dried. The coated member so obtained is positively charged in the darkness by a corona discharge process at 6 KV, exposed through a transparent positive illuminated by an adjacent 100-watt tungsten lamp source located 30 cm from the electrophotographic member for 0.5 seconds. The latent electrostatic image so obtained is developed employing a developer containing a negatively charged toner to obtain a positive toner image. The developed toner image is fixed by slightly heating to obtain a clear fixed image.

EXAMPLE II

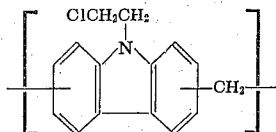
0.2 parts by weight of tetracyanoethylene is added as a sensitizer to the liquid coating composition as prepared in Example I before the coating is employed as an electrophotographic member. The sample thus obtained is subjected to the same charging, exposing, developing and fixing steps as outlined in Example I to obtain a clear fixed image with the exception of employing an exposure time of 0.2 seconds.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used if desirable. In addition, other materials may be incorporated in the system of the present invention which will enhance, synergize or otherwise desirably affect the properties of the systems for their present use.

Anyone skilled in the art will have other modifications occur to him based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. An electrophotographic member comprising a conductive support substrate and superimposed thereon an organic photoconductive film said film comprising an organic photoconductive composition satisfying the formula:



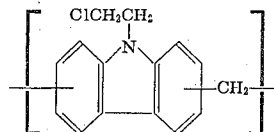
2. An electrophotographic member as defined in

claim 1 further comprising a sensitizer.

3. The electrophotographic member as defined in claim 1 further comprising a plasticizer.

4. An electrophotographic member as defined in claim 1 further comprising an insulating binder resin.

5. An electrophotographic member comprising a conductive support substrate and superimposed thereon an organic photoconductive film said film comprising a solid organic photoconductive composition satisfying the formula:



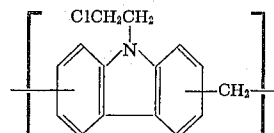
6. The electrophotographic member as defined in claim 5 further comprising a sensitizer.

7. The electrophotographic member as defined in claim 5 further comprising a plasticizer.

8. The electrophotographic member as defined in claim 5 further comprising an insulating binder resin.

9. An electrophotographic imaging process comprising

a. providing an electrophotographic member, said member comprising a conductive support substrate having superimposed thereover an organic photoconductive film said film comprising a solid organic photoconductive composition satisfying the formula:



b. applying a substantially uniform electrostatic charge in the dark to the surface of said film; and

c. selectively dissipating said charge by exposure of the charged surface of said film to activating electromagnetic radiation, thus forming a latent electrostatic image on the surface of said film.

10. The imaging process of claim 9, wherein the latent electrostatic image is rendered visible by development with finely divided electroscopic marking material.

11. An electrophotographic process as defined in claim 5 wherein said electrophotographic member is sensitized said sensitizer being selected from the group consisting of tetracyanoethylene, tetracyanoquinodimethane, chloranil, bromanil, alpha-naphthoquinone, anthraquinone, methylene blue, crystal violet, and malachite green.

12. The process as defined in claim 5 wherein said electrophotographic composition further comprises a plasticizer said plasticizer being selected from the group consisting of chlorinated paraffin, phosphate plasticizers and phthalate plasticizers.

13. The process as defined in claim 5 wherein said electrophotographic member is cascade developed.

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