Aug. 15, 1972 A. J. GUARNACCIO 3,684,506
DIMERIC POLY-N-VINYL CARBAZOLE ORGANIC PHOTOCONDUCTOR
AND PHOTOCONDUCTIVE ELEMENTS EMBODYING SAME
Filed Aug. 24, 1970

FIG. 1

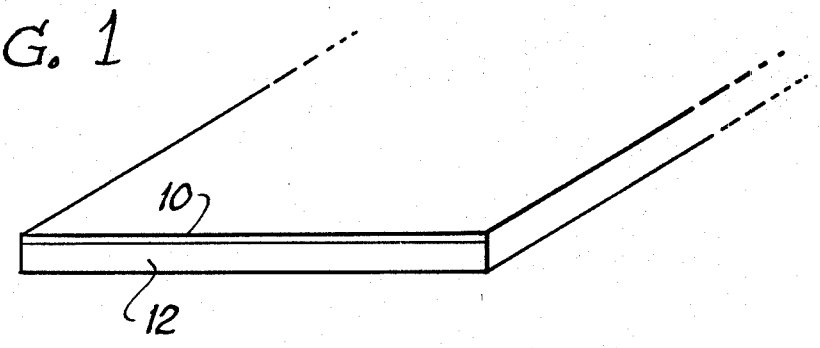


FIG. 2

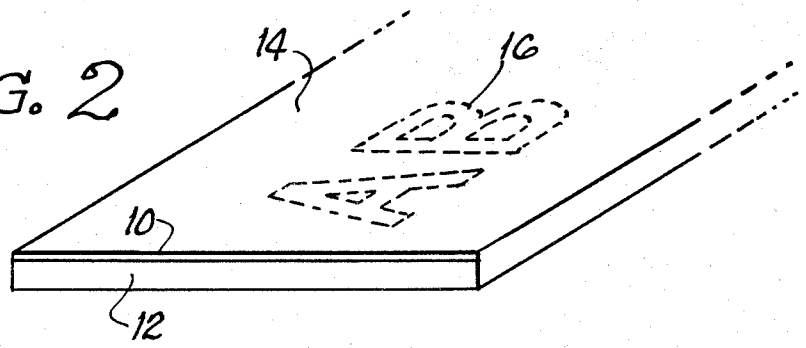
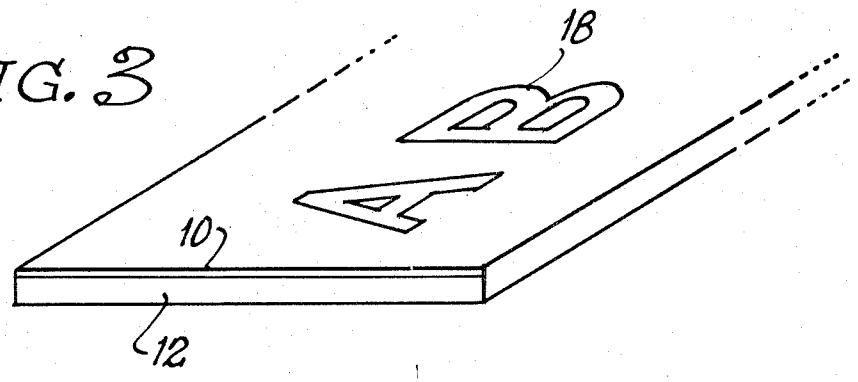


FIG. 3



United States Patent Office 3,684,506
Patented Aug. 15, 1972

3,684,506

DIMERIC POLY-N-VINYL CARBAZOLE ORGANIC PHOTOCONDUCTOR AND PHOTOCONDUCTIVE ELEMENTS EMBODYING SAME

Anthony J. Guarnaccio, 8015 Wisner, Niles, Ill. 60648, and Robert N. Dreyer, Rte. 1, Box 652, Kenosha, Wis. 53140

Continuation-in-part of application Ser. No. 612,432, Jan. 30, 1967. This application Aug. 24, 1970, Ser. No. 66,432
(Filed under Rule 47(a) and 35 U.S.C. 116)
Int. Cl. G03g 5/06
U.S. Cl. 96—1.6 15 Claims

ABSTRACT OF THE DISCLOSURE

The invention is addressed to the preparation of an electrophotographic element having a photoconductive layer formulated of an organic photoconductor in the form of an alkenyl carbazole dimer and in which the electrophotographic element can be processed for imaging purposes in the conventional manner for electrostatic printing.

This is a continuation-in-part of copending application Ser. No. 612,432, filed Jan. 30, 1967, now abandoned.

This invention relates to an electrophotographic composition and material and to a photoconductive coating formed thereof for use in the preparation of an image by electrostatic or xerographic technique.

A well known electrostatic imaging process, generally referred to as the Xerox process and described in the Carlson Pat. No. 2,297,691, involves an element carrying a photoconductive layer which is given a blank electrostatic charge under subdued light or in the dark, as by ion transfer from a corona discharge, followed by an exposure to light modulated by an image, as by projection of a photographic image. The illuminated areas of the charged photoconductive layer are discharged to leave a latent electrostatic image on the layer. The resultant electrostatic image can then be developed, as by dusting with an electroscopic powder, such as a pigmented resinous powder carrying an opposite electrostatic charge, as described in U.S. Pats. Nos. 2,618,551; 2,788,288; or 2,940,934. Instead, development can be achieved by a liquid developer of the type described in U.S. Pats. Nos. 2,877,133, 2,891,911, and 2,907,674. The powder or pigment of the powder or liquid developer adheres to the electrostatically charged latent image. The resulting developed image can be used in a number of ways. It can be fixed thereon to form the image on the photoconductive layer or it can be transferred from the photoconductive layer to a copy sheet for fixing.

A widely used electrostatic process, such as described in the Grieg Pat. No. 3,052,539, or in the Middleton Pat. No. 3,121,006, utilizes as the electrophotographic element ordinary paper as the conductive base having a photoconductive coating of zinc oxide which forms a layer having a conductivity of at least 10^{-10} ohm^{-1} cm.$^{-1}$ in the absence of illumination and a decay factor of less than 3.0.

Such inorganic photoconductors are limited in their application and use. For example, the applied coatings are not transparent and they are thus limited in their manner of exposure to produce the latent electrostatic image.

In order to achieve copy of good quality, it is necessary for the photoconductive coating of inorganic photoconductors to be provided in heavy coating weights thereby to increase the cost of the coating and materially to increase the weight and stiffness of the sheet. In addition, layers formed of inorganic photoconductors are handicapped by surface sensitivity to hard objects.

It is an object of this invention to produce an electrophotographic material formulated of an organic substance which can be formulated to produce a new and improved photoconductive layer which can be employed in layers of low coating weight; which is relatively translucent or transparent to light; which has little surface sensitivity to hard objects; which can be used in conventional electrostatic copying processes for the preparation of latent electrostatic images that can be developed to produce copy of good quality; in which the coating can be applied in a simple and efficient manner to produce a photoconductive layer having good shelf life and the desired resistivity for use in electrostatic reproduction; which can be formulated as a stable solution in a solvent system; which produces a photoconductive layer that is free of flaking; which is characterized by slow dark decay; which produces a photoconductive layer useful in electrophotography, photoplastic recording, photographic recording and as a lithographic duplicating master.

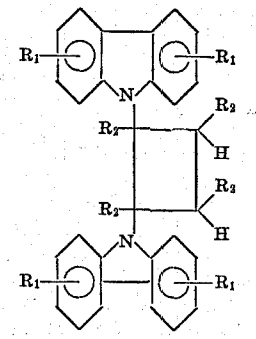
These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of this invention is shown in the accompanying drawing, in which:

FIG. 1 is a perspective view, partially in section, of a photoconductive element embodying the features of this invention;

FIG. 2 is a perspective view similar to that of FIG. 1 showing the photoconductive element with the latent electrostatic image formed thereon; and

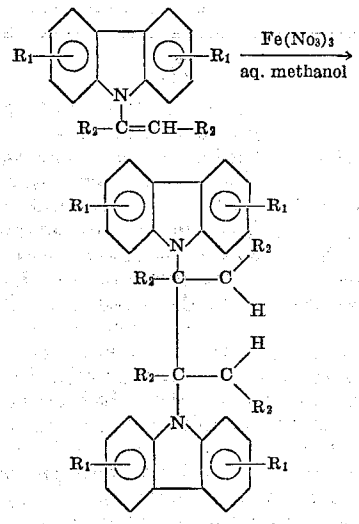
FIG. 3 is a view similar to that of FIGS. 1 and 2 showing the photoconductive element with the image fixed thereon.

It has been found that a dimer of N-alkenyl carbazole can be used as an organic electrophotographic material in the preparation of photoconductive coatings employed in electrostatic copy processes in which the dimer of N-alkenyl carbazole is represented by the formula:



wherein R_1 is hydrogen; an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, pentyl—up to dodecyl; an aryl group such as benzyl, naphthyl, phenanthryl, anthracyl and the like; a cycloalkyl group such as cyclopentyl, cyclohexyl and the like; an alkylaryl group such as xylyl, tolyl, and the like; a cyano group, a carboxylic group or an amino group, and in which R_2 is hydrogen, an alkyl group, an aryl group or a cycloalkyl group of the type described above for R_1. In a preferred compound, both R_1 and R_2 are hydrogen.

The dimers of N-alkenyl carbazoles described above can be prepared in accordance with the method described by McKinley et al. in Journal of Organic Chemistry, 31, pp. 1963–4 (1966). As described by this publication, the N-alkenyl carbazole is dissolved in an aqueous methanol in a ratio of about 9 parts by weight methanol to 1 part by weight water, and ferric nitrate is added. After a few minutes, a crystalline precipitate is formed by the reaction.



wherein R_1 and R_2 are as described above.

It has been found that electrophotographic coatings formulated to include one of the foregoing dimers and a binder can be charged by way of, for example, a corona discharge at a faster rate than organic photoconductors heretofore employed, such as polyvinyl carbazole, when used in an electrostatic copy process.

The organic photoconductive dimer of N-alkenyl carbazole is formulated with a suitable binder for application to form the photoconductive coating **10** on a suitable conductive base sheet **12** such as paper, metal, film, and the like.

As the binder component with which the dimer is combined, use should be made of a material which has a specific conductivity greater than 10^{-12} ohm^{-1} cm.$^{-1}$ and preferably higher than 10^{-10} ohm^{-1} cm.$^{-1}$.

As a representative, it is preferred to make use of a Union Carbide Corporation resin identified as VMCH formulated of 86% vinyl chloride, 13% vinyl acetate and 1% maleic acid, but other resinous binders can be employed, such as butadiene-styrene copolymer 45:55, organo silicon resins, such as Dow-Corning DC–996, a polystyrene, acrylic and methacrylic ester polymers, such as Acryloid A–10, chlorinated rubber, such as Parlon, and alkyd resins, such as General Electric Glyptol 2469.

In the combination of dimer and resin, the materials can be employed in the ratio of 1 part by weight dimer to 0.1–10 parts by weight resin and preferably with the materials present in about equal parts by weight. The materials can be formulated into a suitable coating composition reduced to the desired viscosity with a compatible organic solvent, such as the ketones, esters and aromatic hydrocarbons, in which a desired coating viscosity can be achieved with a solid content within the range of 5–25% by weight.

By way of modification, the light sensitivity of the dimer can be increased by the combination to include electron affinitive molecules, such as tetracyanoethylene, chloranil and the like; acid activators, such as carboxylic acids; mineral acids, such as hydrochloric acid, nitric acid and the like, or metal halides, such as boron chlorides, phosphorus chlorides and the like; and chemical activators, such as iodoform, carbon tetrabromide and carbonyl containing compounds, such as benzophenone, hydroxybenzophenone and the like. The desired increase in light sensitivity can be achieved when the electron affinitive compound is incorporated into the coating in an amount within the range of 0.005 to 1.0 percent by weight on a solids basis.

By way of still further modification, the spectral sensitivity of the dimer can be extended into the visible part of the spectrum by the addition of dye sensitizers, such as triaryl methane dyes, xanthene dyes, thiazine dyes, acridine dyes, and the like. For this purpose, it is desirable to make use of a dye sensitizer in an amount within the range of 0.005 to 1.0 percent by weight of the coating on a solids basis.

The following are examples of coating compositions embodying the features of this invention and which may be applied on a suitable conductive base sheet, such as paper to produce an electrophotographic element capable of being imaged by conventional electrostatic technique.

EXAMPLE 1

N-vinyl carbazole dimer	g.	1.0
Vinyl chloride (86)-vinyl acetate (13)-maleic acid (1) resin (VMCH)	g.	1.0
Methylene chloride solvent	cc.	20

EXAMPLE 2

N-vinyl carbazole dimer	g.	1.0
VMCH resin	g.	1.0
Methylene chloride solvent	cc.	20
1% solution in methanol of Rhodamine B dye	cc.	0.5

EXAMPLE 3

N-propenylcarbazole dimer	g.	1.0
Silicone resin—Dow DC–996	g.	1.0
Toluene	cc.	20
1% solution of chloranil	cc.	0.5

EXAMPLE 4

N-styryl carbazole dimer	g.	1.0
Polyvinyl acetate resin	g.	1.0
Acetone	cc.	20
Dichloroacetic acid	cc.	0.0002
Rhodamine dye	cc.	0.0002

The composition of Examples 1 to 4 is coated onto the surface of a suitable base sheet, such as paper, by conventional coating techniques such as flow coating, roller coating and the like. The amount of coating applied can be varied over a fairly wide range although it is preferable to make use of a relatively light coating such as a coating weight within the range of ¼ to 10 pounds per 3,000 square feet of surface area and preferably of about ½ to 5 pounds per 3,000 square feet of surface area. The applied coating can be allowed to air dry but drying can be accelerated by exposure of the coated sheet to elevated temperature in the order of 100–250° F.

The layer **10** that is formed on the base sheet **12** is a good photoconductive coating which will accept and retain an overall electrostatic charge when sprayed by corona discharge from a conventional source under subdued light. When the charged layer is exposed to light, the charge becomes dissipated in the exposed portions **14** and is retained in the unexposed portions to define a latent electrostatic image **16** which can be developed by conventional liquid or powder developers of the types previously described.

The organic photoconductor permits exposure to be made by reflex or by shoot-through as well as projection to produce the latent electrostatic image for subsequent development.

The developed image **18** can be set on the layer for direct copy or the powdered image can be transferred to a copy sheet by charge reversal or by direct contact whereafter the image is set on the copy sheet. When the photoconductive layer is applied onto the surface of a suitable lithographic master, an imaged master can be produced when the developed image is set on the plate or the powdered image can be transferred from the photoconductive layer to the surface of a lithographic plate for imaging the duplicating master for use in the production of multiple copies by lithographic duplicating technique.

Thus, in use, the coated sheet is first bombarded in subdued light by corona discharge to spray the surface of the layer with an electrostatic charge. The charge is

received and held by the photoconductive coating **10**. The charged sheet is then exposed to light modulated by projection of a photographic image whereby the photoconductive coating is rendered conductive in the exposed areas to enable dissipation of the electrostatic charge while the charge is retained in the unexposed areas to define the latent electrostatic image **16**.

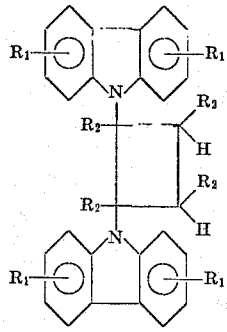
The imaged layer is then dusted with a developing electroscopic powder or by a liquid developer whereby the pigmented resinous particles of the developing composition are attracted to the latent electrostatic image for development. The particles can be set by heat to fix the image **18** or transferred to a copy sheet for setting thereon.

It will be apparent that we have provided a new and improved electrophotographic element which can be used in electrostatic copy processes for the development of images by electrostatic technique.

It will be further understood that changes may be made in the details of formulation and construction without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. An electrophotographic recording element comprising a base sheet and a coating on the surface of the base sheet containing an organic binder and an alkenyl carbazole dimer having the formula:



in which R_1 is a group selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, alkylaryl, cyano, carboxyl and amino and R_2 is a group selected from the group consisting of hydrogen, alkyl, aryl and cycloalkyl.

2. An electrophotographic recording element as claimed in claim **1** in which the alkenyl carbazole dimer is present in the coating in combination with an organic binder having a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

3. An electrophotographic recording element as claimed in claim **1** in which the organic binder and alkenyl carbazole dimer are present in the coating in the ratio of 1 part by weight dimer to 0.1–10 parts by weight binder.

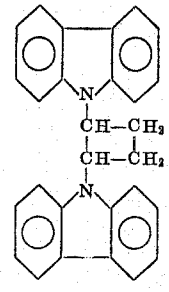
4. An electrophotographic recording element as claimed in claim **2** in which the coating includes a compound that broadens the spectral sensitivity of the dimer, said compound being selected from the group consisting of triaryl methane dye, xanthene dye, thiazine dye and acridine dye, said compound being present in an amount within the range of 0.005 to 1.0 percent by weight of the coating.

5. An electrophotographic recording element as claimed in claim **2** in which the coating includes a compound to increase the light sensitivity of the dimer, said compound selected from the group consisting of tetracyanoethylene, chloranil, a carboxylic acid, a mineral acid, an acidic metal halide, iodoform, carbon tetrabromide, benzophenone and hydroxy benzophenone, and being present in an amount sufficient to increase the light sensitivity of the dimer.

6. An electrophotographic recording element as claimed in claim **5** wherein said compound is present in an amount within the range of .005 to 1% by weight of the said coating.

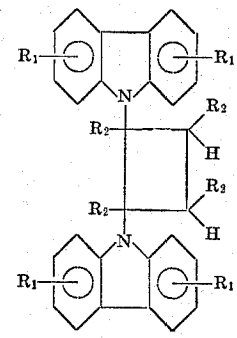
7. An electrophotographic recording element as claimed in claim **1** wherein R_1 is hydrogen.

8. An electrophotographic recording element as claimed in claim **1** wherein the dimer has the formula



and is present in the said coating on the base sheet with an organic binder having a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

9. In the method of preparing copies by electrostatic copy process, the steps of charging by corona discharge onto an electrophotographic element having a transparent to translucent photoconductive coating on a conductive base sheet in which the photoconductive coating contains an N-alkenyl carbazole dimer having the formula:



in which R_1 is a group selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, alkylaryl, cyano, carboxyl and amino and R_2 is a group selected from the group consisting of hydrogen, alkyl, aryl and cycloalkyl, exposing the charged coating to a light pattern whereby the charge dissipates from the exposed areas and is retained in the unexposed areas to define a latent electrostatic image, and then contacting the image with a developer containing an electroscopic pigment to develop the image.

10. The method as claimed in claim **9** in which the alkenyl carbazole dimer is present in the coating in combination with an organic binder having a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

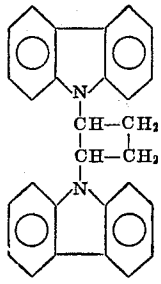
11. The method as claimed in claim **10** in which the coating contains a compound that broadens the spectral sensitivity of the dimer and is present in an amount within the range of 0.005 to 1 percent by weight, said compound being a dyestuff selected from the group consisting of a triaryl methane dye, xanthene dye, thiazine dye and acridine dye.

12. The method as claimed in claim **10** in which the coating includes a compound to increase the light sensitivity of the dimer, said compound selected from the group consisting of tetracyanoethylene, chloranil, a carboxylic acid, a mineral acid, an acidic metal halide, iodoform, carbon tetrabromide, benzophenone and hydroxy benzophenone, and being present in an amount sufficient to increase the light sensitivity of the dimer.

13. The method as claimed in claim **12** wherein said compound is present in an amount within the range of .005 to 1% by weight of the said coating.

14. The method as claimed in claim **9** wherein R_1 is hydrogen.

15. The method as claimed in claim 9 wherein the dimer has the formula



and is present in the coating on the base sheet with an organic binder having a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

References Cited

UNITED STATES PATENTS

3,037,861 6/1962 Hoegl ..... 96—1.5

OTHER REFERENCES

McKinley et al.: J. Org. Chem., 31, 1963–64 (1966).

JOHN C. COOPER III, Primary Examiner

U.S. Cl. X.R.

96—1.5, 1 PC; 252—501; 260—315

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,506 Dated August 15, 1972

Inventor(s) Anthony J. Guarnaccio and Robert N. Dreyer

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

IN THE SPECIFICATION

In column 1, line 34, delete "blank" and insert therefor -- blanket --.

Signed and sealed this 29th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks