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NOVEL PHOTOCONDUCTIVE CARBOZALE POLYMERS AND PHOTOCONDUCTIVE ELEMENTS EMBODYING SAME

Filed March 2, 1970

FIG. 1

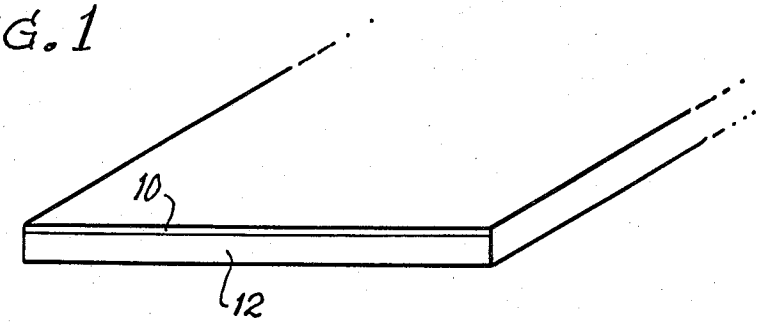


FIG. 2

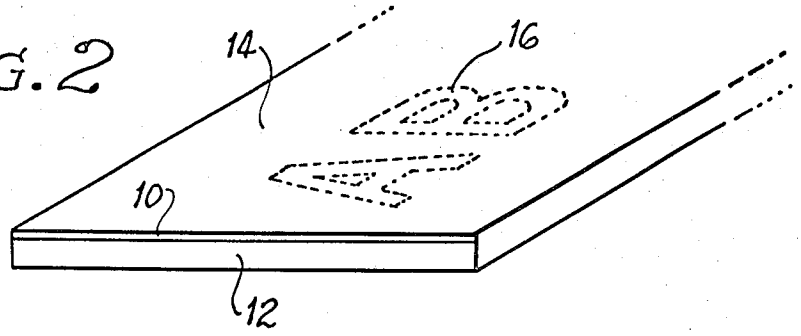
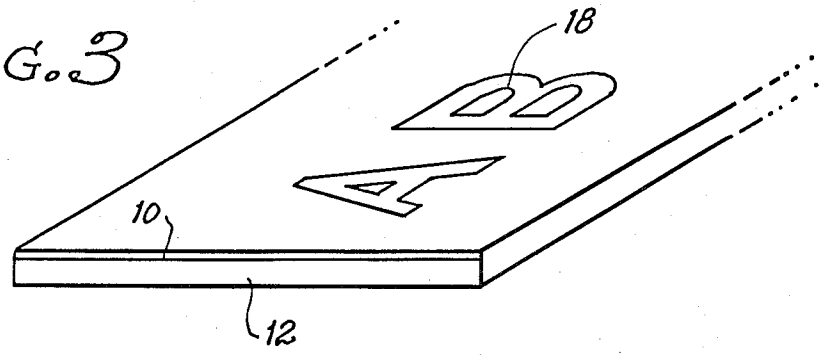


FIG. 3



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NOVEL PHOTOCONDUCTIVE CARBAZOLE POLYMERS AND PHOTOCONDUCTIVE ELEMENTS EMBODYING SAME

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ABSTRACT OF THE DISCLOSURE

This invention is addressed to novel substituted N-vinyl carbazole polymers and copolymers and to the preparation of an electrophotographic element having a photoconductive layer formulated of same.

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 blanket 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.

In copending application Ser. No. 612,432, filed Jan. 30, 1967, and entitled "Organic Photoconductor and Photoconductive Elements Embodying Same" now abandoned, description is made of an electrophotographic recording element and an electrostatic copy process using same wherein the recording element contains a surface

coating comprising an organic binder and the dimer of an N-alkenyl carbazole. The use of a photoconductor in the form of an N-alkenyl carbazole dimer represents a significant improvement over the use of inorganic photoconductors, such as zinc oxide, in that the dimer may be employed in low coating weights and provide recording elements which are capable of broad commercial application. However, the organic photoconductor coatings described in the aforementioned application are frequently incapable of attaining the speeds characteristic of inorganic photoconductors.

It is accordingly an object of the present invention to produce an electrophotographic material which has speeds comparable to those of inorganic photoconductors, but which have all of the advantages of organic photoconductors, such as capability of application in low coating weights, relative absence of surface sensitivity to hard objects, good shelf life and resistance to decay.

It is a related object of the invention to produce an electrophotographic material formulated of an organic component which can be formulated to produce a new and improved photoconductive layer which is free from flaking, which is characterized by slow dark decay and which produces a photoconductive layer useful in electrophotographic photoplastic recording, photographic recording and as a lithograph duplicating master.

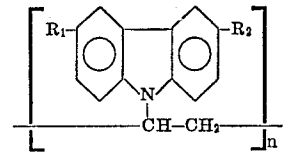
These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of this invention is shown in the accompanying drawing, in which:

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.

The concepts of the present invention reside in new and improved polymers and copolymers formed of substituted N-vinyl carbazoles which can be formulated alone, or with a binder component, to provide a coating on a base sheet to form an electrophotographic recording element. The substituted N-vinyl carbazole polymers which serve as the photoconductive material in accordance with the present invention are poly N-vinyl carbazoles having a recurring unit of the formula:



wherein R_1 is a substituent which functions as an electron donor to donate electrons to the aromatic nucleus on which it is substituted, and R_2 is a substituent selected from the group consisting of an alkyl group having 1–12 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, etc., dodecyl; an aryl having 6–20 carbon atoms, such as phenyl, benzyl, naphthyl, phenanthryl, anthracyl, etc.; a cycloalkyl having 4–8 carbon atoms, such as cyclobutyl, cyclopentyl, cyclohexyl, etc.; halogen including fluorine, chlorine, bromine and iodine; or hydrogen.

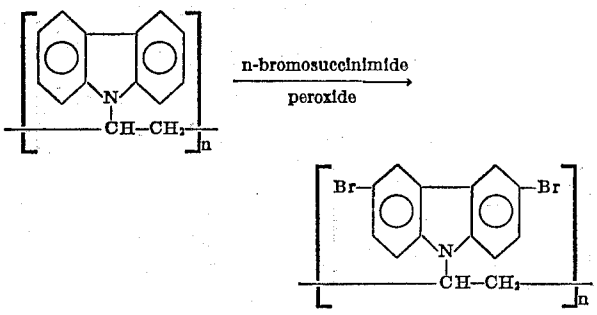
While the novel substituted polyvinyl carbazoles of the present invention have been described above as hav-

ing the R_1 substituent in the 6 position and the R_2 substituent in the 3 position, it will be understood by those skilled in the art that the present invention also contemplates those polyvinyl carbazoles wherein the recurring unit contains the R_1 substituent in the 3 position and the R_2 substituent in the 6 position on the carbazole molecule.

Substituents which operate as electron donors when present on an aromatic nucleus are known to those skilled in the art, and generally include those substituents which deactivate an aromatic nucleus by donating electrons thereto to thereby render the aromatic nucleus less susceptible to nucleophilic aromatic substitution. Such substituents generally include alkyl groups having 1–12 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, etc.; aryl groups having 6–20 carbon atoms, such as phenyl, benzyl, naphthyl, phenanthryl, anthracyl, etc.; thioalkyl groups where the alkyl group contains 1–6 carbon atoms, such as thiomethyl, thioethyl, thiopropyl, etc.; thioaryl groups where the aryl group contains 6–15 carbon atoms, such as thiophenyl, thiobenzyl, thionaphthyl, etc.; cycloalkyl groups having 4–8 carbon atoms such as cyclobutyl, cyclopentyl, cyclohexyl, etc.; alkoxy groups having 1–6 carbon atoms, such as methoxy, ethoxy, propoxy, butoxy, etc.; hydroxy groups and amino groups. In accordance with the practice of the present invention, R_1 is preferably an alkyl or aryl substituent as described above.

Without limiting the invention as to theory, it is believed that the efficiency of the substituted vinyl carbazole polymers of the invention as improved electrophotoconductive materials is due at least in part to the tendency of the substituents on the aromatic ring of the carbazole nucleus to donate electrons to the nucleus, thereby imparting to the aromatic nucleus a partial electrical charge to increase the electrical conductivity of the polymers.

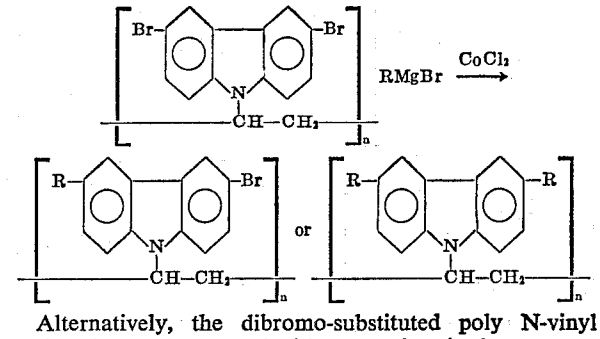
The new and improved photoconductors of the present invention can be prepared by a variety of methods. For example, it is possible to brominate poly N-vinyl carbazole dissolved in an organic solvent with a brominating agent, such as N-bromosuccinimide in the presence of a peroxide catalyst to produce the mono and dibrominated product, as follows:



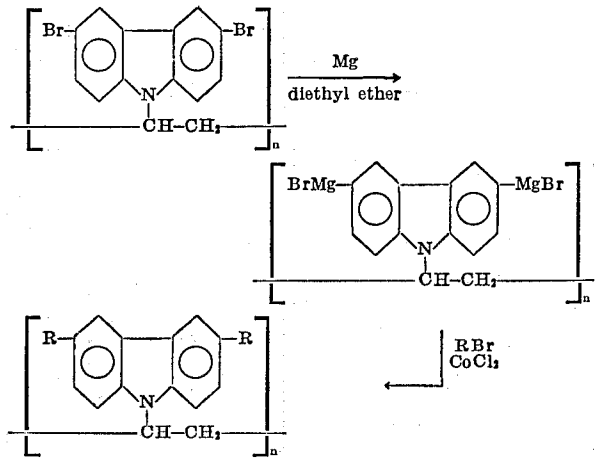
The foregoing reaction may be carried out by dissolving poly N-vinyl carbazole in a solvent, including benzene, nitrobenzene, chlorobenzene, dimethyl formamide, dioxane, as well as a variety of others, and carrying out the reaction at a temperature within the range of 60–110° C. for 1 to 5 hours in the presence of a peroxide free radical initiator such as benzoyl peroxide.

Thereafter, the resulting bromide or dibromide may be reacted with an alkyl magnesium bromide or an aryl magnesium bromide in the presence of cobalt chloride to form the corresponding bromo-alkylated or arylated carbazole or the corresponding di-substituted carbazole,

depending upon the proportions of the reactants, as follows:



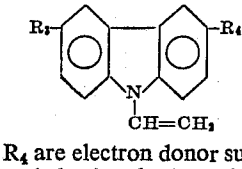
Alternatively, the dibromo-substituted poly N-vinyl carbazole may be reacted with magnesium in the presence of anhydrous diethyl ether to form a Grignard intermediate, which can then be reacted with an alkyl or aryl bromide to form the resulting di-substituted polyvinyl carbazole, as illustrated by the following equations:



The N-vinyl carbazole polymers which may be used to prepare the novel photoconductors of the present invention are preferably high molecular weight, film forming resins. Suitable poly N-vinyl carbazoles are available under the trademark "Luvican" and include "Luvican K323," "Luvican M170" and "Luvican K260."

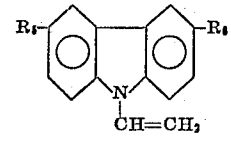
It will be understood by those skilled in the art that it is similarly possible to utilize one or more of the above reaction schemes for reaction with monomeric N-vinyl carbazole to form the corresponding substituted monomer, which can then be polymerized in a conventional manner, such as by heating to a temperature within the range of 120–175° C. or by reaction with a peroxide free radical initiator.

In accordance with another concept of the present invention, the photoconductors may be in the form of a copolymer of a vinyl carbazole of the formula:



(I)

wherein R_3 and R_4 are electron donor substituents, and another vinyl carbazole having the formula:



(II)

wherein R_5 and R_6 are electron withdrawing substituents. It has been found that copolymers of these carbazoles have a very high photoconductivity which, without limit-

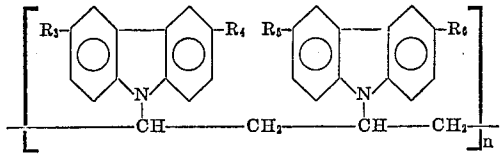
ing the invention as to theory, is believed to be due at least in part to the tendency of the electron-rich carbazole molecule containing electron donor substituents R_3 and R_4 to transfer electron to the electron-deficient carbazole molecule containing electron withdrawing substituents R_5 and R_6 to thereby increase the photoconductivity of the polymer.

The electron donor substituents R_3 and R_4 can be any of a variety of substituents known to have the effect of donating electrons to an aromatic nucleus, and include amino groups, hydroxy groups, alkoxy groups having 1–6 carbon atoms, such as methoxy, ethoxy, propoxy, butoxy, etc.; alkyl groups having 1–12 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, etc.; aryl groups having 6–20 carbon atoms; such as phenyl, benzyl, naphthyl, phenanthryl, anthracyl, etc.; thioalkyl groups where the alkyl group contains 1–6 carbon atoms, such as thiomethyl, thioethyl, thiopropyl, etc.; thioaryl groups where the aryl group contains 6–15 carbon atoms, such as thiophenyl, thiobenzyl thionaphthyl, etc.

The electron withdrawing groups R_5 and R_6 may be any of a variety of organic groups known by those skilled in the art to exhibit a tendency to withdraw electrons from an aromatic nucleus, and include nitro groups, cyano groups, carboxy groups, halogen (including fluorine, chlorine, bromine and iodine) and sulfonic acid groups. It is frequently preferred that R_5 and R_6 be nitro groups or cyano groups.

Copolymers of one or more of each of the carbazoles represented by Formulas I and II can be formed by conventional polymerization techniques, such as by thermal polymerization at a temperature of 110° and 180° C. for a period of 1 to 5 hours, or by polymerization in the presence of a peroxide (e.g. benzoyl peroxide) at a temperature of 30 to 90° C. for 1 to 5 hours. The relative proportion of the carbazole monomers in the copolymer are not critical, although the monomer having the Formula II above and containing the electron withdrawing substituents preferably constitutes between 1.0 and 60.0% by weight of the copolymer.

In preparing the novel copolymers in accordance with this concept of the invention, it is generally preferred to employ a substantially equimolar proportion of each of the monomers. It has been found that the use of equimolar portions results in very regular orientation of the monomer molecules in the copolymers whereby the copolymers essentially comprise a copolymer having recurring units of the formula:



The new and improved photoconductors of the present invention may be applied to a suitable conductive base, such as paper, either with or without the use of a binder component since the novel polymers of the present invention are polymers which are film forming resins. Thus, referring to FIG. 1, the novel polymers and copolymers of the present invention are applied to form a photoconductive coating **10** on suitable conductive base sheet **12**, including paper, metal, film or the like.

In accordance with the preferred practice of the present invention, the novel polymers and copolymers of this invention are combined with a suitable binder to form the photoconductive coating **10** on the base sheet **12**. As the binder component with which the polymers and copolymers of the invention are combined, use can be made of a material which has a specific conductivity lower than 10^{-12} ohm^{-1} cm.$^{-1}$, and preferably higher than 10^{-10} ohm^{-1} cm.$^{-1}$.

A wide variety of binder components may be used in accordance with this embodiment of the present invention. Illustrative of such binders are Union Carbide resin VMCH, which is a resin formulated of 86% vinyl chloride, 13% vinyl acetate and 1% maleic acid, butadiene-styrene copolymers, and preferably those wherein the weight ratio between butadiene and styrene is about 45:55, organic silicon resins, such as Dow-Corning DC–996, polystyrenes, acrylic and methacrylic ester polymers, such as Acryloid A–10, chlorinated rubber, such as Parlon and alkyd resins, such as G.E. Glptal 2469.

In formulating the novel polymers and copolymers of the present invention, with a binder component, the materials can be employed in the ratio of 1 part by weight of the polymer or copolymer to 0.1–10 parts by weight of the binder component, and preferably with the materials being 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 ketones, esters, aromatic hydrocarbons, as well as a variety of others, in which a desired coating viscosity can be activated with a solids content within the range of 5–20% by weight.

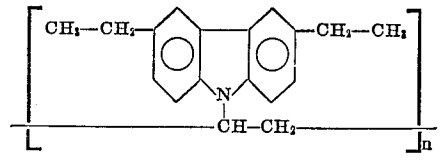
By way of modification, the light sensitivity of the polymers and copolymers can be increased by the combination to include electron affinitive molecules such as tetracyanoethylene, chloranil and the like; acid activators such as carboxylic acids; mineral acids such as hydrochloric acid, nitric acid 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, hydroxyphenone 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 polymers and copolymers 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.

Having disclosed the basic concept of the invention, reference is now made to the following examples which are provided by way of illustration, and not by way of limitation, of the invention.

EXAMPLE 1

This example illustrates the preparation of a polyvinyl carbazole of the formula:



Fifty grams of poly-9-vinyl carbazole (Luvican M–170) are dissolved in 1000 grams of chlorobenzene. To the solution are added 93 grams of n-bromosuccinimide and 1.0 gram of benzoyl peroxide, and the resulting mixture is heated to 80° C. for a period of 3 hours.

The resulting polymer is crystallized in methanol, and analysis reveals that the product is the 3,6-dibromo derivative.

The dibrominated product is then redissolved in fresh chlorobenzene and reacted with a stoichiometric amount of ethyl magnesium bromide in the presence of a small

amount of $CoCl_2$ for a period of 1 hour at 60° C. The product is crystallized in methanol, and is found to be the 3,6-diethyl derivative of 9-vinyl carbazole.

The following examples illustrate the use of the polyvinyl carbazole prepared in Example 1 in coating compositions which may be applied to a suitable conductive base sheet to produce an electrophotographic element embodying the features of the present invention.

EXAMPLE 2

	Grams
Poly(3,6-diethyl-9-vinyl carbazole)	1.0
Methylene chloride	26.0

EXAMPLE 3

	Grams
Poly(3,6-diethyl-9-vinyl carbazole)	1.0
Vinyl chloride-vinyl acetate-maleic acid terpolymer resin (VMCH—Union Carbide)	1.0
Methylene chloride	26.0

EXAMPLE 4

Poly(3,6-diethyl-9-vinyl carbazole)	gram	1.0
VMCH resin	do	1.0
Acetone solvent	cc	20
1% solution in methanol of Rhodamine B dye	cc	0.5

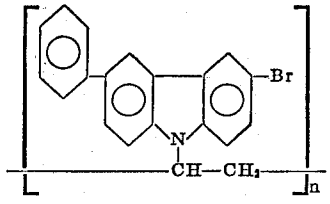
EXAMPLE 5

Poly(3,6-diethyl-9-vinyl carbazole	gram	1.0
Silicon resin—Dow DC996	do	1.0
Toluene solvent	cc	70
1% solution of chloramid	cc	0.5

The compositions of Examples 2–5 may be applied by conventional techniques, such as flow coating, roll coating and the like to provide a coating weight within the range of 0.25–10 lbs. per 3000 sq. ft. of surface area, or 0.5–5 lbs. per 3000 sq. ft.

EXAMPLE 6

This example illustrates the preparation of a polyvinyl carbazole having the general formula:



Polyvinyl carbazole (Luvican M–170) is brominated in the manner described in Example 1 to provide the 3,6-dibromo product. Thereafter, the dibrominated carbazole is dissolved in bromobenzene and is reacted with phenyl magnesium bromide in the presence of $CoCl_2$ at 90° C. for 3 hours. The product is crystallized in methanol.

Analysis reveals that the product is poly(3-bromo-6-phenyl-9-vinyl carbazole).

The carbazole polymer prepared in Example 6 may be formulated into coating compositions for use in preparing electrophotographic recording elements, as illustrated by the following examples.

EXAMPLE 7

Poly(3-bromo-6-phenyl-9-vinyl carbazole)	gram	1.0
Methylene chloride solvent	cc	22

EXAMPLE 8

Poly(3-bromo-6-phenyl-9-vinyl carbazole)	gram	1.0
Polyvinyl acetate resin	do	1.0
Rhodamine dye	cc	.0002
Acetone solvent	cc	20

EXAMPLE 9

Poly(3-bromo-6-phenyl-9-vinyl carbazole)	gram	1.0
VMCH resin	do	1.0
1% solution of chloramid	cc	0.5
Acetone solvent	cc	20

The coating compositions of Examples 7 to 9 can be applied to a base sheet in the manner described with reference to Examples 2 to 5.

EXAMPLE 10

This example illustrates the preparation of poly(3,6-diisopropyl-9-vinyl carbazole).

Polyvinyl carbazole is brominated with n-bromo-succinimide in the manner described in Example 1 to produce the dibrominated product. Thereafter, the dibromo compound is dissolved in diethyl ether and reacted with magnesium at 40° C. for a period of 4 hours to produce the corresponding Grignard reagent.

The Grignard reagent is then reacted with isopropyl bromide in a molar ratio of 1 mole of the carbazole Grignard compound to 2 moles of isopropyl bromide. The resulting product is purified in methanol, and analysis confirms that it is the 3,6-diisopropyl derivative of the polymer.

The foregoing polymer can then be formulated into a coating composition of the type described in Examples 2 to 5 and 7 to 9 for use in producing an electrophotographic recording element embodying the features of the present invention.

EXAMPLE 11

This example illustrates the preparation of poly(3-isopropyl-9-vinyl carbazole).

Poly 9-vinyl carbazole is brominated with n-bromosuccinimide in the presence of benzoyl peroxide using 20 grams of polyvinyl carbazole, 18.5 grams of n-bromosuccinimide and .18 gram of benzoyl peroxide.

Analysis shows that the monobrominated product is produced.

The foregoing polymer is then reacted with isopropyl magnesium bromide in the presence of a small amount of cobalt chloride, and the resulting product is confirmed as being the isopropyl derivative of polyvinyl carbazole, which can be formulated into coating compositions of the type described in Examples 2 to 5.

EXAMPLE 12

This example illustrates the preparation of a copolymer of 3,6-diethyl-9-vinyl carbazole with 3,6-dinitro-9-vinyl carbazole.

3,6-diethyl-9-vinyl carbazole is prepared by brominating 25 grams of 9-(2-chloroethyl) carbazole dissolved in glacial acetic acid with 17 grams of potassium bromide dissolved in water and 25 grams of potassium bromate. The mixture is then maintained at 30° C. for a period of 4 hours, after which the mixture is poured over ice and left overnight. Thereafter, the crude product was filtered and purified by crystallization. Analysis reveals that the product is 3,6-dibromo-9-(2-chloroethyl)carbazole.

The above carbazole is then dehydrochlorinated by dissolving it in ethanol, and alcoholic KOH is added to the solution. The resulting mixture is then refluxed for 2 hours, and the product is filtered and purified.

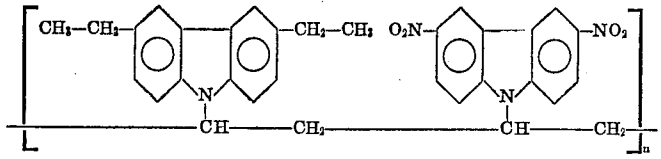
Analysis reveals it to be 3,6-dibromo-9-vinyl carbazole.

The dibrominated carbazole is then reacted with ethyl magnesium bromide in the presence of cobalt chloride, and the resulting product is 3,6-diethyl-9-vinyl carbazole.

Equimolar amounts of 3,6-dinitro-9-vinyl carbazole, prepared by initiation of 9-vinyl carbazole with nitric acid in the presence of sulfuric acid, and 3,6-diethyl-9-vinyl carbazole are polymerized by dissolving the monomers in chlorobenzene and adding to the mixture benzoyl peroxide. The reaction mixture is maintained at 80° C. for

2.5 hours, and the resinous product is separated and purified.

Analysis reveals the polymer to be recurring units of the formula:



The copolymer preapred in Example 12 may be formulated into various coating compositions for use in coating a suitable conductive base to produce an electrophotographic recording element embodying the features of this invention, as illustrated by the following examples:

EXAMPLE 13

	Grams
Substituted vinyl carbazole copolymer	1.0
Methylene chloride	26.0

EXAMPLE 14

	Grams
Substituted vinyl carbazole copolymer	1.0
Vinyl chloride-vinyl acetate-maleic acid terpolymer resin	1.0
Methylene chloride	26.0

EXAMPLE 15

Substituted vinyl carbazole copolymer	gram	1.0
VMCH resin	do	1.0
Acetone solvent	cc	20
1% solution in methanol of Rhodamine B dye	cc	0.5

EXAMPLE 16

Substituted vinyl carbazole	gram	1.0
Silicon resin—Dow DC996	do	1.0
Toluene solvent	cc	70
1% solution of chloramid	cc	0.5

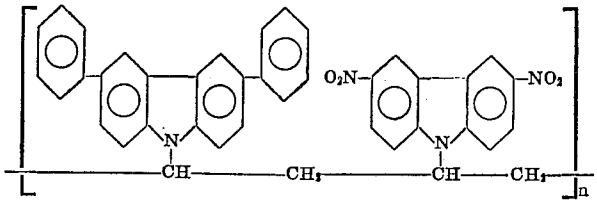
The compositions of Examples 13 to 16 can be applied to a suitable base sheet in accordance with the methods described with reference to Examples 2 to 5.

EXAMPLE 17

This example illustrates the preparation of a copolymer of 3,6-diphenyl-9-vinyl carbazole and 3,6-dinitro-9-vinyl carbazole.

3,6-dibromo-9-vinyl carbazole, prepared in the manner described in Example 12, is reacted with phenyl magnesium bromide for 3 hours at 50° C. The resulting product is 3,6-diphenyl-9-vinyl carbazole.

A copolymer of equimolar amounts of 3,6-diphenyl-9-vinyl carbazole and 3,6-dinitro-9-vinyl carbazole is prepared in the same manner described in Example 12. The resulting product is a polymer having a recurring unit with the formula:



The foregoing copolymer can then be formulated into a coating composition of the type described in Examples 2 to 5, 7 to 9 and 13 to 15.

EXAMPLE 18

This example illustrates the preparation of a copolymer of 3,6-diamino-9-vinyl carbazole and 3,6-dicyano-9-vinyl carbazole.

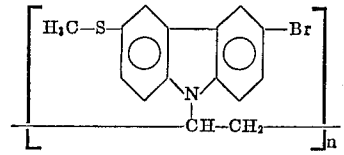
3,6 - dibromo - 9(2 - chloroethyl)carbazole is prepared in the manner described in Example 12, and is thereafter dissolved in dimethyl formamide and the mixture is refluxed in sodium cyanide for 5 hours. The product is 3,6-dicyano-9(2-chloroethyl) carbazole.

A portion of the dicyano carbazole is dehydrochlorinated in the manner shown in Example 12, to produce 3,6 - dicyano - 9 - vinyl carbazole and the balance is reacted with hydrogen at 100 p.s.i.g. for 2 hours at 95° C. The resulting product of the hydrogenation reaction is 3,6 - diamino - 9 - (2 - chloroethyl) carbazole, which is then dehydrochlorinated. The product is 3,6-diamino-9-vinyl carbazole.

A copolymer is prepared from substantially equimolar amounts of the diamino carbazole and the dicyano carbazole in the manner described in Example 12. The product is separated and purified. This copolymer may then be formulated into a coating composition for use in preparing an electrophotographic recording element in the manner described in Examples 2 to 5.

EXAMPLE 19

This example illustrates the preparation of a polyvinyl carbazole having a recurring unit of the formula:



Polyvinyl carbazole is brominated in the manner described in Example 1 to provide the 3,6-dibromo product. Thereafter, the dibrominated carbazole is dissolved in dimethyl formamide, and refluxed with methyl mercaptan in the presence of a copper oxide catalyst for 2 hours.

The resulting product is found to be poly(3-bromo-6-thiomethyl)-9-vinyl carbazole.

Analogous thioalkyl and thioaryl derivatives of vinyl carbazole and polyvinyl carbazole by using similar alkyl or aryl mercaptans can be prepared in a manner described in Example 19.

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 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 I have provided new and improved photoconductive polymers and copolymers which can be employed to provide improved electrophotographic elements for use in electrostatic copy processes for the development of images by electrostatic techniques. The novel photoconductive polymers and copolymers of the present invention have all of the advantages of inorganic photoconductors, such as high speed of development, without the frequent disadvantages of such inorganic photoconductors, such as sensitivity to hard objects and the like.

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

I claim:

1. An electrophotographic recording element comprising a base sheet and a photoconductive coating on the base sheet comprising a copolymer of (A) 3,6-diphenylvinylcarbazole and (B) 3,6-dinitrovinylcarbazole.

2. An element as defined in claim **1** wherein the coating includes from 0.005 to 1 percent by weight of a compound to increase the light sensitivity of the copolymer selected from the group consisting of tetracyanoethylene, chloranil, iodoform, carbon tetrabromide, benzophenone, hydroxy benzophenone, a carboxylic acid, a mineral acid and an acidic metal halide.

3. An element as defined in claim **2** wherein the coating includes from 0.005 to 1.0% by weight of a compound to broaden the spectral sensitivity of the copolymer selected from the group consisting of a triaryl methane dye, xanthene dye, thiazine dye and an acridine dye.

4. An element as defined in claim **1** wherein (B) constitutes between 1.0 and 60% by weight of said copolymer.

5. An element as defined in claim **1** wherein said polymer is present in the coating in combination with an organic binder for a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

6. An element as defined in claim **5** in which the organic binder and said polymer are present in the coating in the ratio of 1 part by weight polymer to 0.1–10 parts by weight binder.

7. In a method of preparing copies by an electrostatic copy process, the steps of charging by corona discharge onto an electriphotographic element having a transparent to translucent photoconductive coating on a conductive base sheet in which the photoconductive coating contains a copolymer of (A) 3,6-diphenylvinylcarbazole (B) 3,6-dinitrovinylcarbazole, exposing the charged coating to a light pattern whereby the charge dissipates from the exposed areas to define a latent electrostatic image, and then contacting the image with a developer containing an electroscopic pigment to develop the image.

8. The method as defined in claim **7** in whcih the polymer is present in the coating in combination with an organic binder having a specific conductivity of at least 10^{-12} ohm^{-1} cm.$^{-1}$.

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96—1 PC; 252—501; 260—88.3