

[54] **ORGANIC PHOTOCONDUCTOR FOR ELECTROPHOTOGRAPHY**
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[51] **Int. Cl.** **G03g 5/06, G03g 7/00**
[58] **Field of Search**..... **96/1.5; 260/315**

[56] **References Cited**

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[57] **ABSTRACT**
Photoconductive materials are prepared from an N-aryl carbazole compound and a Lewis acid. The materials are charge transfer complexes with the N-aryl carbazole such as N-phenylcarbazole acting as an electron donor and the Lewis acid such as 2, 4, 7-trinitro-9-fluorenone acting as an electron acceptor. The molar ratio of the donor to the acceptor can be in the range from 1:0.5 to 1:1.

3 Claims, No Drawings

ORGANIC PHOTOCONDUCTOR FOR ELECTROPHOTOGRAPHY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an organic photoconductive composition comprising N-aryl carbazole and more particularly to the use of N-aryl carbazole in combination with a nitrofluorenone and their use in electrophotographic processes.

2. Description of the Prior Art

The forming and developing of images on the surfaces of certain photoconductive materials by electrostatic means is now well known. Carlson, in U.S. Pat. No. 2,297,691 teaches the basic xerographic process, which involves uniformly charging a photoconductive insulating layer and then exposing the layer to a light-and-shadow image which dissipates the charge on the portions of the layer which are exposed to light. The electrostatic latent image formed on the layer corresponds to the configuration of the light-and-shadow image. In another modification, a latent electrostatic image is formed on the photoconductive insulating layer by charging the layer in image configuration. A finely divided developing material comprising a colorant called a toner and a toner carrier is deposited on the image layer. The developing material is normally attracted to those portions of the layer which retain a charge, thereby forming a powder image corresponding to the latent electrostatic image. The powder image may then be transferred to paper or any other receiving surface. The powder image is permanently bonded to the paper by any suitable fixing means. Typically, a heating process, called fusing, is used, as described in U.S. patents such as U.S. Pat. Nos. 2,357,809, 2,891,011 and 3,079,342.

It is possible to employ a wide variety of photoconductive insulating materials in the electrostatic process. For example, Carlson, in U.S. Pat. No. 2,297,691 discloses photoconductive insulating materials such as anthracene, sulfur, selenium or mixtures thereof.

These materials generally have sensitivity in the blue or near ultraviolet range, and all but selenium have a further limitation of being only slightly light sensitive. For this reason, selenium has been the most commercially accepted material for use in electrophotographic plates. Vitreous selenium, however, while desirable in most aspects, suffers from serious limitations in that its spectral response is somewhat limited to the ultraviolet, blue and green region of the spectrum, and the preparation of vitreous selenium plates requires costly and complex procedures, such as vacuum evaporation. Also, selenium plates require the use of a separate conductive substrate layer, preferably with an additional barrier layer deposited thereon before deposition of the selenium photoconductor. Because of these economic and commercial considerations, there have been many recent efforts towards developing photoconductive insulating materials other than selenium for use in electrophotographic plates.

It has been proposed that various two-component materials be used in photoconductive insulating layers used in electrophotographic plates. For example, the use of inorganic photoconductive pigment dispersed in suitable binder materials to form photoconductive insulating layers is known. It has further been demonstrated that organic photoconductive insulating dyes

and wide variety of polycyclic compounds may be used together with suitable resin materials to form photoconductive insulating layers useful in binder-type plates. In each of these two systems, it is necessary that at least one original component used to prepare the photoconductive insulating layer be, itself, a photoconductive insulating material.

In a third type plate, inherently photoconductive polymers are used; frequently in combination with sensitizing dyes or Lewis acids to form photoconductive insulating layers. Again, in these plates at least one photoconductive insulating component is necessary in the formation of the layer. While the concept of sensitizing photoconductors is itself commercially useful, it does have the drawback of being limited to only those materials already having substantial photoconductivity.

The above discussed three types of known plates are further described in U.S. Pat. Nos. 2,999,750; 3,037,861; 3,041,165; 3,072,479; 3,097,095; 3,113,022; 3,126,281; 3,159,483; 3,237,119; 3,484,237; 3,607,258; Canadian Pat. No. 644,167 and German Pat. No. 1,068,115.

The polymeric and binder-type organic photoconductor plates of the prior art generally have the inherent disadvantages of high cost of manufacture, brittleness, and poor adhesion to supporting substrates. A number of these photoconductive insulating layers have low temperature distortion properties which make them undesirable in an automatic electrophotographic apparatus which often includes powerful lamps and thermal fusing devices which tend to heat the xerographic plate. Also, the choice of physical properties has been limited by the necessity of using only inherently photoconductive materials.

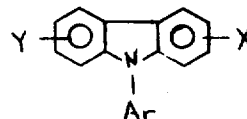
Inorganic pigment-binder plates are limited in usefulness because they are often opaque and are thus limited to use in systems where light transmission is not required. Inorganic pigment-binder plates have the further disadvantage of being non-reusable due to high fatigue and rough surfaces which make cleaning difficult. Still another disadvantage is that the materials used have been limited to those having inherent photoconductive insulating properties.

SUMMARY OF THE INVENTION

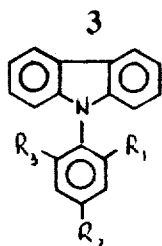
It is an object of the invention to provide a composition which is photoconductive and can readily be processed so as to form a photoconductive structure.

It is another object of this invention to provide a photoconductive insulating material devoid of the above noted disadvantages.

It has now been found that the problems of the prior art can be overcome through the use of a Lewis acid, preferably trinitro-fluorenone in combination with N-aryl carbazole characterized by the following formula:



wherein X and Y are each selected from the group consisting of H, Cl, Br and NO and wherein Ar is selected from the group consisting of phenyl, naphthyl and phenanthryl. The phenyl is advantageously a substituted phenyl having the following structural formula:



wherein:

R_1 and R_3 are selected from the group consisting of H, NO_2 and COOH ;

R_2 is selected from the group consisting of H, $\text{N}(\text{CH}_3)_2$, C_6H_5 , NO_2 , $\text{o}-\text{NO}_2-\text{CH}_2\text{H}_4-\text{NH}$, $\text{o}-\text{NH}_2-\text{C}_6\text{H}_4-\text{NH}$, and Br.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The photoconductive material adaptable for use in electrophotographic processes includes an electron donor and an electron acceptor in the form of a charge transfer complex. While the mechanism of the complex chemical interreaction involved in the present process is not completely understood, it is believed that a "charge transfer complex" is formed having absorption bands characteristic of neither of the two components considered individually. The mixture of the two non or poorly photoconductive components seems to have a synergistic effect which is much greater than additive.

The electron acceptor may be any suitable Lewis acid and the preferred group of Lewis acids are 2, 4, 7-trinitro-9-fluorenone; 2, 4, 5, 7-tetranitro-9-fluorenone; 2, 6-dichloro-p-benzoquinone; 2, 5-dinitro-9-fluorenone; 1,5-dichloro-2, 4-dinitrobenzene; 2, 5-dichloro-p-benzoquinone; 2, 3, 6-trichloro-p-benzoquinone; 2-chloro-3, 5-dinitropyridine; 2, 4, 5, 7, 9-pentanitroindene; 2, 1-alpha 7-fluorene-11, 12-dione; 2, 5-diphenyl-p-benzoquinone; 2, 3-dichloro-1, 4-naphthoquinone; 9-dicyanomethylene-2, 4, 7-trinitrofluorene. Of these the most preferred are 2, 4, 7-trinitro-9-fluorenone and 2, 4, 5, 7-tetranitro-9-fluorenone. These two electron acceptors give substantially increased electrophotographic speed over those listed above or with respect to Lewis acids in general.

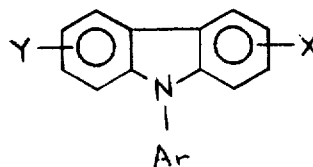
Other typical Lewis acids are: quinones, such as P-benzoquinone, chloranil, naphthoquinone-(1,4), 2,3-dichloronaphthoquinone-(1,4), anthraquinone, 2-methylantraquinone, 1,4-dimethylantraquinone, 1-chloroanthraquinone, anthraquinone-2-carboxylic acid, 1,5-dichloroanthraquinone, 1-chloro-4-nitroanthraquinone, phenanthrenequinone, acenaphthenequinone, pyranthrenequinone, chrysenequinone, thio-naphthenequinone, anthraquinone-1,8-disulfonic acid and anthraquinone-2-aldehyde; triphthaloylbenzene-aldehydes such as bromal, 4-nitrobenzaldehyde, 2,6-dichlorobenzaldehyde-9, 2-ethoxy-1-naphthaldehyde, anthracene-9-aldehyde, pyrene-3-aldehyde, oxindole-3-aldehyde, pyridine-2,6-dialdehyde, biphenyl-4-aldehyde; organic phosphonic acid such as 4-chloro-3-nitrobenzene-phosphonic acid, nitrophenols, such as 4-nitrophenol, and picric acid; acid anhydrides, for example, acetic-anhydride, succinic anhydride, maleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, perylene-3,4,9,10-tetracarboxylic acid and chrysene-2,3,8,9-tetracarboxylic anhydride, di-bromo maleic acid anhydride, metal halides of the metals and metalloids of the groups IB, II through to group VIII of the periodical

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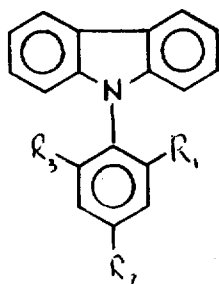
system, for example: aluminum chloride, zinc chloride, ferric chloride, tin tetrachloride, (stannic chloride), arsenic trichloride, stannous chloride, antimony pentachloride, magnesium chloride, magnesium bromide, calcium bromide, calcium iodide, strontium bromide, chromic bromide, manganous chloride, cobaltous chloride, cobaltic chloride, cupric bromide, ceric chloride, thorium chloride, arsenic tri-iodine; boron halide compounds, for example: boron trifluoride, and boron trichloride; and ketones, such as acetophenone, benzophenone, 2-acetylnaphthalene, benzil, benzoin, 5-benzoyl acenaphthene, biacene-dione, 9-acetyl-anthracene, 9-benzoyl-anthracene, 4-(4-dimethyl-amino-cinnamyl)-1-acetylbenzene, acetoacetic acid anilide, indandione-(1,3), 1,3-diketo-hydrindene, acenaphthene quinonedichloride, anisil, 2,2-pyridil and furil.

Additional Lewis acids are mineral acids such as the hydrogen halides, sulphuric acid and phosphoric acid; organic carboxylic acids, such as acetic acid and the substitution products thereof, monochloro-acetic acid, dichloroacetic acid, trichloro-acetic acid, phenylacetic acid, and 6-methylcoumarinylacetic acid (40); maleic acid, cinnamic acid, benzoic acid, 1-(4-diethyl-amino-benzoyl)-benzene-2-carboxylic acid, phthalic acid, and tetra-chlorophthalic acid, alpha-beta-dibromo-beta-formyl-acrylic acid (mucobromic acid), dibromomaleic acid, 2-bromo-benzoic acid, gallic acid, 3-nitro-2-hydroxyl-1-benzoic acid, 2-nitro phenoxy-acetic acid, 2-nitrobenzoic acid, 4-nitro-benzoic acid, 3-nitro-4-ethoxy-benzoic acid, 2-chloro-4-nitro-1-benzoic acid, 3-nitro-4-methoxy-benzoic acid, 4-nitro-1-methyl-benzoic acid, 2-chloro-5-nitro-1-benzoic acid, 3-chloro-6-nitro-1-benzoic acid, 4-chloro-3-nitro-1-benzoic acid, 5-chloro-3-nitro-2-hydroxybenzoic acid, 4-chloro-2-hydroxy-benzoic acid, 2,4-dinitro-1-benzoic acid, 2-bromo-5-nitro-benzoic acid, 4-chlorophenyl-acetic acid, 2-chlorocinnamic acid, 2-cyanocinnamic acid, 2,4-dichlorobenzoic acid, 3,5-dinitro-benzoic acid, 3,5-dinitro-salicylic acid, malonic acid, mucic acid, acetosalicylic acid, benzilic acid, butane-tetracarboxylic acid, citric acid, cyano-acetic acid, cyclo-hexane-dicarboxylic acid, cyclo-hexanecarboxylic acid, 9,10-dichloro-stearic acid, fumaric acid, itaconic acid, levulinic acid (levulic acid), malic acid, succinic acid, alpha-bromo-stearic acid, citraconic acid, dibromo-succinic acid, pyrene-2,3,7,8-tetra-carboxylic acid, tartaric acid; organic sulphonic acids, such as 4-toluene sulphonic acid, and benzene sulphonic acid, 2,4-dinitro-1-methyl-benzene-6-sulphonic acid, 2,6-dinitro-1-hydroxy-benzene-4-sulphonic acid, 2-nitro-1-hydroxybenzene-4-sulphonic acid, 4-nitro-hydroxy-2-benzene sulphonic acid, 3-nitro-2-methyl-1-hydroxy-benzene-5-sulphonic acid, 6-nitro-4-methyl-1-hydroxy-benzene-2-sulphonic acid, 4-chloro-1-hydroxy-benzene-3-sulphonic acid, 2-chloro-3-nitro-1-methylbenzene-5-sulphonic acid and 2-chloro-1-methyl-benzene-4-sulphonic acid.

The electron donor is an N-aryl carbazole characterized by the following formula:



wherein X and Y are selected from the group consisting of H, Cl, Br and NO, and wherein Ar is selected from the group consisting of phenyl, naphthyl and phenanthryl. The phenyl is advantageously a substituted phenyl having the following structural formula:



wherein:

R₁ and R₃ are selected from the group consisting of H, NO and COOH;

R₂ is selected from the group consisting of H, N(CH₃)₂, C₆H₅, NO₂, o-NO₂-C₆H₄-NH, o-NH₂-C₆H₄-NH, and Br.

The following table sets forth advantageous combinations for R₁, R₂ and R₃.

Formulation	R ₁	R ₂	R ₃
a	H	H	H
b	NO ₂	H	H
c	H	NO ₂	H
d	COOH	H	H
e	COOH	H	COOH
f	H	N(CH ₃) ₂	H
g	H	C ₆ H ₅	H
h	H	o-NO ₂ -C ₆ H ₄ -NH	H
i	H	o-NH ₂ -C ₆ H ₄ -NH	H
j	H	Br	H

Advantageously, the photoconductor complex includes a crystallization prevention agent. The agent is a carbazoyl compound preferably a dicarbazoyl cycloalkane such as dicarbazoyl cyclobutane.

EXAMPLE I

A standard trinitrofluorenone/N-phenyl carbazole solution was prepared by dissolving 2 grams (8.17 × 10⁻³ mole) of N-phenyl carbazole in 3 milliliters (ml.) of tetrahydrofuran and mixing the solution with a solution of 2.6 grams (8.25 × 10⁻³ mole) of trinitrofluorenone dissolved in 19 ml. of tetrahydrofuran.

The solution is then coated on an aluminized Mylar substrate by a doctor-blade technique to a thickness of 0.2 mil. The coatings crystallize almost immediately upon curing. However, even though crystallized the coating had a charge acceptance of 300 volts and 12 seconds of exposure to a 10 foot candle light source were required to reduce this voltage by half (t_{1/2} = 120 foot candle sec).

EXAMPLE II

The conditions of Example I were repeated except that 0.3 gm (0.77 × 10⁻³ mole) of dicarbazoyl cyclobutane (6percent by weight) was added to the standard solution.

A 0.3 mil coating was produced. The coating did not crystallize upon curing, and had a charge acceptance of 900 volts with a t_{1/2} = 3.2 foot candle sec. The dicar-

bazoyl cyclobutane thus acted as a crystallization prevention agent.

EXAMPLE III

The conditions of Example I were followed except that the formulation comprised 22 ml. of tetrahydrofuran, 2.6 gm. of trinitrofluorenone, 2 gm. of N-phenyl carbazole and 1 gram of Monsanto RP 1323 as a binder. The charge acceptance was 520 volts and the t_{1/2} was 5.4 foot candle sec (fcs.).

EXAMPLE IV

The conditions of Example III was followed except that 2 gm of the binder was used. The charge acceptance was 1000 volts and the t_{1/2} was 12 f.c.s.

EXAMPLE V

The standard solution of Example I was added 10 grams of a solution of 10 grams of poly N-vinyl carbazole (sold under the trademark Luvican by BASF Co.) in 100 ml. of tetrahydrofuran.

The solution was then coated on an aluminized Mylar substrate, by a doctor-blade technique, producing a 0.4 mil coating. The sample was tested in a Victoreen apparatus and was found to have a charge acceptance of 1200 volts and required 1.5 seconds to reduce the potential to one half of its original value using a 1 foot candle light (t_{1/2} = 1.5 fcs). A 0.4 mil coating tested in a commercial xerographic copier, gave 1,500 copies of good quality.

EXAMPLE VI

A standard solution was prepared as described in Example I. Three ml. of a solution of 10 grams of polystyrene (sold under the trademark PS 3, by Dow Chemical Co.) in 30 ml. of tetrahydrofuran was mixed with the standard solution and a 0.2 mil coating was applied to an aluminized Mylar substrate.

The charge acceptance was found to be 450 volts, and the t_{1/2} = 3.2 fcs.

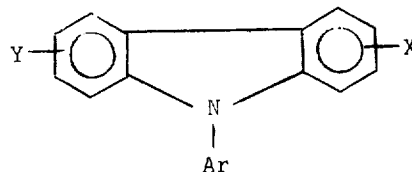
EXAMPLE VII

The procedure of Example V was followed except that 1 gram of solution polyester 49000 (sold by Du Pont) was mixed with the standard solution.

A 0.3 mil coating was found to have a t_{1/2} = 50 fcs, and a charge acceptance of 500 volts.

What is claimed is:

1. A photoconductive electrically insulating composition comprising a charge transfer complex of a Lewis acid and an N-aryl carbazole, characterized by the structural formula:



wherein X and Y are each selected from the group consisting of N, Cl, Br, and NO; wherein Ar is selected from the group consisting of phenyl, naphthyl and phenanthryl; wherein said Lewis acid is taken from the group consisting of 2,4,7-trinitro-9-fluorenone; 2,4,5,7-tetranitro-9-fluorenone; 2,6-dichloro-p-benzoquinone; 2,5-dinitro-9-fluorenone; 1,5-dichloro-2,4-dinitrobenzene; 2,5-dichloro-p-benzoquinone; 2,3,6-

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trichloro-p-benzoquinone; 2-chloro-3, 5-dinitropyridine; 2,4,5,7,9-pentanitroindene; 2,1-alpha 7-fluorene-11, 12-dione; 2,5-diphenyl-p-benzoquinone; 2,3-dichloro-1, 4-naphthoquinone; 3-dicyanomethylene-2,4,7-trinitro-fluorene; and the molar ratio of the N-aryl carbazole to the Lewis acid is in the range of 1:0.5 to 1:1 and there is included a dicarbazolyl cycloalkane in an amount sufficient to prevent crystallization of the composition.

2. The composition defined in claim 1 wherein said dicarbazolyl cycloalkane is dicarbazolyl cyclobutane.

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3. A photoconductive electrically insulating composition comprising a charge transfer complex of an electron acceptor taken from the group consisting of 2,4,7-trinitro-9-fluorenone and 2, 4, 5, 7-tetranitro-9-fluorenone and an electron donor as N-phenyl carbazole, the ratio of electron acceptor to donor being from 5:1 to 1:1 and including dicarbazolyl cyclobutane in an amount sufficient to prevent crystallization of said composition.

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