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ELECTROPHOTOGRAPHIC MATERIALS COMPRISING POLYMERIC INTRAMOLECULAR CHARGE TRANSFER COMPLEXES

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ABSTRACT OF THE DISCLOSURE

An electrophotographic material comprising an organic photoconductive compound consisting of a vinyl monomer unit carrying an aromatic and/or heterocyclic substituent capable of being of being an electron donor and a vinyl monomer unit carrying an aromatic and/or heterocyclic substituent capable of being an electron acceptor.

Electrophotography is a copying method which combines an electrostatic and a photoconductive phenomenon. In spite of advantages of a conventional silver salt photographic method with respect to sensitivity, resolving power and image quality, etc., the method cannot satisfy requirements of high speed recording and precise copying technique because of difficulties in controlling a high speed treatment and processing, since the method is substantially composed of chemical and wet processes. Electrophotography is a process to reproduce a copy physically or electrically and is a dry process which eliminates such defects. In practical use, there is known xerography method which employs a selenium photosensitive plate, and Electrofax method which uses zinc oxide dispersed in a resinous matrix. In addition to the above materials, inorganic substances such as zinc sulfide, cadmium sulfide and the like, and organic substances such as anthracene, anthraquinone, carbazole and perylene, etc., are known as useful substances for photoconductive materials. Recently, a series of heterocyclic compounds (U.S. Patents 3,041,165, June 26, 1962; 3,066,023, Nov. 27, 1962), and a poly-N-vinylcarbazole mixture (U.S. Patent 3,037,861, June 5, 1962), have been disclosed by Kalle A.G., Germany. However, these substances are insufficient for all requirements such as practicality, reliability, stability, easy handling, and high speed processing, and also are not sufficient for recent copying materials which are used in various fields.

This invention relates to the composition of the photosensitive material having photoconductivity which is to be employed for electrophotography. The following compounds enable the production of photosensitive material having excellent sensitivity and stability, and represented by the general formula

—D—A—D—A—D—D—

in which A and D are arranged alternatively or arranged at an appropriate interval and D and A represent a monomer unit for an electron donor and for an electron acceptor respectively.

A general principle to facilitate a selection of compounds having photoconductivity has not been known in the literature of organic photosensitive material for electrophotography. Much effort has been given to experimental selection of appropriate photosensive materials from numerous organic compounds. Further, a photoconductive layer having a practical sensitivity has been obtained by combining an appropriate sensitizer with a photoconductor. In the general formula set forth above, the

present inventors have found a definite principle applicable to a photoconductive compound for electrophotography, and thereby obtained high sensitive photoconductive substance in accordance with the principle of the present invention.

Generally, in a classification of organic semiconductors, some of them can be classified as charge-transfer molecular complexes. For example, they are the complexes of polynuclear aromatic compound and halogen molecule, the complexes of polynucleic aromatic compound and tetracyano compound, the complexes of dimethyl aniline or N,N-tetramethyl phenylene diamine and chloranil or bromanil and the like. The conductivity of the charge-transfer complex compounds may be explained by the fact that transport of electrons is promoted in a complex of charge transfer type which is produced by the combination of molecule having electron donor and molecule having electron acceptor.

The present invention has introduced such conception to a conductive mechanism of photosensitive materials for electrophotography. Further, improvement of efficiency is accomplished by polymerizing respective monomer units for an electron donor and an electron acceptor into high polymers in which both units are stereoregularly arranged at adequate distance from each other. That is, a resistivity of such material is sufficiently high for electrophotography in the dark, and resistivity decreases with the intensity of light applied. The photoconductor for electrophotography of the present invention is a high polymer and has a film forming ability by itself. Thus a layer applied to a support has a high resolution as the layer is homogeneous and sufficiently even. In addition, the photoconductive layer having an excellent light transmission may be obtained by applying the photoconductive layer on a transparent support.

The sensitivity of the photoconductive substance for electrophotography of the present invention may be improved by incorporation of an appropriate sensitizer.

The examples for a monomer unit of the electron donor of the present invention are as follows:

Acenaphthylene, 5-aminoacenaphthylene, 3-aminoacenaphthylene, 5-N,N-dimethylaminoacenaphthylene, 5-N,N-diethylaminoacenaphthylene, 5-methylacenaphthylene, 3-ethylacenaphthylene, N-vinylcarbazole, N-vinyl-3-aminocarbazole, N-vinyl-3-N',N'-dimethylaminocarbazole, 1-vinylnaphthalene, 2-vinylnaphthalene, 9-vinylanthracene, styrene, and cumarone, etc.

These are polynuclear aromatic compounds which are able to polymerize or compounds having a substituted group of electron donor such as amino group or N-dimethylamino group.

The examples of the monomer units for an electron acceptor are as follows:

4-nitrostyrene, 5-nitroacenaphthylene, 5-cyanoacenaphthylene, N-vinyl-3-nitrocarbazole, 1-vinyl-3-nitronaphthalene, vinylanthraquinone and the like. These are the polynuclear aromatic compounds substituted by a group of an electron acceptor.

Of course, the function of each monomer unit as an electron donor or an electron acceptor is in a strength relative to each other. Therefore, they must be selected in view of said relative strength.

The following are detailed illustrations for such compounds. Nitrated polyacenaphthylene whose 5–45% of acenaphthene group is nitrated may be produced by adding an appropriate quantity of concentrate nitric acid dropwise at 20°–75° C. after polyacenaphthylene is dissolved in a mixed solvent of chlorobenzene and glacial acetic acid.

This is a compound in which acenaphthene and nitroacenaphthene recur alternatively or are arranged in an

appropriate position. The former is a monomer unit for an electron donor and the latter is a monomer unit for an electron acceptor. An excellent photoconductivity is brought about by an electron transport between each unit.

A compound having a similar structure may be obtained by polymerization of 5-nitroacenaphthylene and acenaphthylene. The efficiency is quite identical with the above compound.

By a partial reduction of poly-5-nitroacenaphthylene, 10–80 mole percent of nitro group contained therein is reduced to amino group and a compound in which 5-nitroacenaphthylene and 5-aminoacenaphthylene recur alternately, or are arranged in an appropriate position, may be produced. In this compound, the former is a monomer unit for an electron acceptor and the latter is a monomer unit for an electron donor. A compound having a similar structure may be obtained by a polymerization of 5-nitroacenaphthylene and 5-aminoacenaphthylene. The efficiency is quite identical with the above compound.

Polyaminoacenaphthylene is dimethylated by dimethyl sulfate. Nitrated polyacenaphthylene containing 25 mole percent of a nitro group is reduced to aminopolyacenaphthylene similarly to prior arts. The final product is a copolymer of N,N-dimethylaminoacenaphthylene and acenaphthylene. The former is a monomer unit for an electron donor and the latter is a monomer unit for an electron acceptor and this compound shows an excellent photoconductivity.

A photosensitive material having an excellent sensitivity may be obtained by a polymerization of N-vinylcarbazole and 20–80 mole percent of 5-nitroacenaphthylene. It has been known that poly-N-vinylcarbazole can be used as a photosensitive material for electrophotography. However, the photosensitivity of poly-N-vinylcarbazole is very low. Therefore, the addition of an appropriate sensitizer improves the sensitivity. On the other hand, a copolymer of N-vinylcarbazole and 5-nitroacenaphthylene according to the present invention has a good sensitivity by itself. According to the principle set forth above, the former is a monomer for an electron donor and the latter is a monomer for an electron acceptor and they are placed in appropriate arrangements in a single molecule. The photosensitive property is attributed to an electron transport from a donor unit to an acceptor unit.

A copolymer of N-vinylcarbazole and N-vinyl-3-nitrocarbazole also shows an excellent photosensitivity. This copolymer can be produced by the polymerization of two kinds of monomers or by a partial nitration of poly-N-vinylcarbazole in a mixed solvent of chlorobenzene and gracial acetic acid.

The copolymers of N-vinylcarbazole with either nitrostyrene, vinylnitronaphthalene, or vinylnitroanthracene also show excellent sensitivity.

The compounds set forth above show excellent sensitivity by itself and require no further addition of sensitizer. Of course, the sensitivities of these copolymers may be remarkably improved by the addition of a dyestuff sensitizer.

In forming of the photoconductive layer for electrophotography employing these copolymers, a plasticizer and/or sensitizer is(are) incorporated with these copolymers, if and when necessary, and the resulting solution is applied directly to a support or the surface of polyvinyl acetate film previously coated on a support, and dried to obtain a photoconductive layer.

The addition of the plasticizer results in further improvement in the property of the photoconductive layer. The examples of the plasticizer are: p-terphenyl, diphenyl, diphenyl chloride, β-methyl naphthalene, dioctyl phthalate, triphenyl phosphate, dimethyl glycol phthalate, dibutyl phthalate, and the like.

The plasticizer is added in an amount of 0.5–3.0% (weight).

Dyestuffs known as the sensitizer for an organic photoconductive substance are effective to this invention. The dyestuff sensitizer is added in an amount of 0.01–2% (weight). The examples of the sensitizer are: brilliant green, methyl violet, crystal violet, rhodamine B, rhodamine B extra, rhodamine 6G, rose, Bengal, methylene blue, and alizarin, etc.

Metal plate such as aluminum, zinc, silver, or the like, paper coated with a synthetic resin so as to impregnate no solvent therein, a synthetic resin film whose resistivity is reduced by an antistatic treatment, a synthetic resin film whose resistivity is 10^{2-3} Ω-cm. lower than that of the photoconductive layer, or a film whose specific resistance is less than 10^9 Ω-cm., preferably 10^5 Ω-cm., may be employed as support.

All conventional methods of prior arts may be applied to the process by which an electrophotographic image is produced on the photoconductive layer made by the present invention. Either positive or negative may be charged on the photoconductive layer.

Example 1

10 g. of polyacenaphthylene was dissolved in a mixed solvent of 100 cc. of benzene and 50 cc. of glacial acetic acid. 4 cc. of concentrated nitric acid (d.=1.4) was added dropwise into the resulting solution in 20 minutes while the solution was well stirred and then the temperature was elevated to 70° C. The solution was further heated and stirred for an additional 2 hours. After the reaction was completed a resulting solution was poured into alcohol. Thus a polymer having faint yellow color was produced. This polymer is soluble in benzene, chlorobenzene, or dioxane. According to the organic elementary analysis the nitrogen content of the polymer was 2.53%, and consequently 29.9 mole percent of acenaphthylene group was nitrated.

5 g. of the resulting nitrated polyacenaphthylene was dissolved in 30 cc. of benzene and the solution was applied onto an aluminum plate and dried into a layer of 3μ thickness. Negative charge was applied to the layer by a corona discharge in a conventional manner and followed by a process for exposing the plate to a light from a 100 w. incandescent lamp as a light source through a positive original for 2 seconds. The lamp was spaced 30 cm. from the plate. Subsequent sprinkling of developing powder over the plate resulted in an image having a high resolution, an excellent contrast and a fidelity. The resulting image was fixed by heating at a low temperature.

Example 2

5 g. of the nitrated polyacenaphthylene obtained in the Example 1, 1 g. of diphenyl chloride and 0.02 g. of crystal violet were dissolved in 30 cc. of dioxane. The resulting solution was applied to a paper in the form of layer and dried. After being dried to the free of the solvent, the paper was positively charged by corona discharge. This paper was placed under the original and subjected to exposure of 3,000 luxes for 0.5 second. When developing powder was sprinkled, image of high fidelity was obtained on the plate, and was fixed by heating.

Example 3

10 g. of polyacenaphthylene was dissolved in a mixed solvent of 100 cc. of chlorobenzene and 45 cc. of acetic unhydride. 4 cc. of concentrated nitric acid (d.=1.4) was dropped into the solution in 20 minutes below 30° C., while stirring and then the solution was heated and stirred for 2 hours at 55° C. After the reaction was completed, the resulting solution was poured into alcohol to produce light yellow polymer. An organic elementary analysis showed that the nitrogen content was 3.82% and consequently 47.2 mole percent of acenaphthylene group was nitrated. 5 g. of the resulting nitrated polyacenaphthylene, 1 g. of β-methyl naphthalene and 0.02 g. of rhodamine B were dissolved in 30 cc. of dioxane. The resulting solu-

tion was applied onto an aluminum plate and dried into a 3μ thick layer.

After being negatively charged by a corona discharge in a usual manner, the above plate was placed under a transparent positive original and exposed for 0.5 second to a light from a 100 w. incandescent lamp which was placed about 20 cm. apart. Subsequent sprinkling of a developing powder produced an image having fidelity, excellent resolution and contract. The image was fixed by weak heating.

Example 4

9 g. of acenaphthylene and 4.3 g. of 5-nitroacenaphthylene were dissolved in 25 cc. of benzene in a pressure-proof glass tube and 0.3 g. of an initiator, azo-bis-iso-butylonitril was added. After air in the glass tube was replaced by nitrogen gas, the glass tube was sealed by fusing and was rotated for 12 hours in a thermostat kept at 65° C. After the reaction was completed, the obtained solution was poured into alcohol. Thus a polymer colored in faint yellow was obtained. According to elementary analysis, a nitrogen content was 2.89%. 5 g. of the resulting copolymer and 1.5 g. of diphenyl chloride were dissolved in 30 cc. of dioxane, and the solution was applied to an aluminum plate and dried so as to produce a layer (3μ thick). The treated plate was treated with a corona discharging apparatus adjusted at about 6 kv. and followed by a process for exposing for 1 second to a 100 w. incandescent lamp spaced at a distance of approximately 20 cm., while being superposed with a positive original. Subsequent sprinkling of a developing powder resulted in an image having fidelity, and excellent resolution and contrast. The image was fixed by weak heating.

Example 5

3 g. of poly-5-nitroacenaphthylene obtained by the polymerization of 5-nitroacenaphthylene was dispersed in 20 cc. of concentrated hydrochloric acid and 10 g. of powdered metallic tin was added to the dispersion in step by step at a room temperature. The mixture was reduced for 3 hours while stirring at 100° C. Thus there was produced partially reduced poly-5-nitroacenaphthylene in which approximate 40 mole percent of a nitro group was reduced to an amino group.

2 g. of the resulting partially reduced poly-5-nitroacenaphthylene and 0.2 g. of diphenyl chloride were dissolved in 20 cc. of dimethyl formamide. The solution obtained was applied onto an aluminum plate and dried to produce a layer of 3μ thickness. The treated plate was subjected to a corona discharging in a usual manner and then was exposed for 1 second to a 100 w. incandescent lamp spaced at a distance of about 20 cm., while being superposed with a transparent positive original. Thus an image was produced by weak heating.

Example 6

3 g. of the copolymer (copolymerization ratio 2:3) of 5-nitroacenaphthylene and 5 - dimethylaminoacenaphthylene, and 1 g. of diphenyl were dissolved in 20 cc. of dioxane. The resulting solution was applied onto a cellulose acetate film previously treated antistatically and dried to produce a layer of 3μ thickness. The coated film was subjected to a corona discharging in a usual manner and then was exposed for 2 seconds to 2,000 luxes while being superposed with a transparent positive original. The latent image thus produced was developed by applying a developing powder. Thus an image having fidelity was obtained. This image was fixed by weak heating. This copy can be employed as a second original and many copies may be produced likewise.

Example 7

3 g. of the equimole copolymer of N-vinylcarbazole and acenaphthylene, 0.2 g. of diphenyl chloride and 0.01 g. of crystal violet were dissolved in 30 cc. of benzene. The resulting solution was applied to an aluminum plate and dried to produce a layer of 3μ thickness. The coated plate was subjected to a coronal discharge in a usual manner and then was exposed for 3 seconds to 3,000 luxes while being superposed with a transparent positive original. A latent image thus produced was developed by applying a developing powder and clear image was obtained.

Example 8

2 g. of N-vinylcarbazole and 1 g. of 5-nitroacenaphthylene were dissolved in 25 cc. of benzene in a pressure-proof glass tube and benzoyl peroxide was added as an initiator. The glass tube was sealed by heating after the air in the tube was replaced by nitrogen gas. The contents were heated for 8 hours at 65° C. Then the contents were poured into alcohol. Thus a polymer was produced.

2 g. of the resulting copolymer was dissolved in 20 cc. of chlorobenzene and the solution was applied onto an aluminum plate and dried to produce a layer of 2μ thickness. The coated plate was subjected to a negative charging and then was exposed for 1.5 seconds employing a 125 w. mercury lamp spaced at a distance of 30 cm. while being superposed with a transparent positive original. A copying image having fidelity was produced by sprinkling a developing powder.

In comparison with this copolymer, poly-N-vinylcarbazole was dissolved in chlorobenzene and the resulting solution was applied to an aluminum plate in a manner similar to that indicated above. The coated plate is subjected to exposure of 20 seconds for producing a punctual image. That is, the increment of approximate sixteen times in sensitivity was realized by copolymerizing N-vinylcarbazole with 5-nitroacenaphthylene.

Example 9

Poly-N-vinylcarbazole was dissolved in a mixed solvent of chlorobenzene and glacial acetic acid, and concentrated nitric acid in 50% amount of the calculated quantity was added to the solution drop by drop. The solution was heated for 3 hours at 45° C. and then poured into alcohol. Thus nitrated poly-N-vinylcarbazole was produced. 3 g. of the resulting compound was dissolved in 20 cc. of chlorobenzene and was applied to a paper to produce a photosensitive layer of 2μ thickness after drying. The coated paper was subjected to a negative charging by a corona discharge according to a conventional procedure, and was thereafter exposed for 1.5 seconds under 2,000 luxes while being superposed with a transparent positive original. The latent image thus produced was then developed. An image having fidelity to the original was obtained.

Example 10

4 g. of N-vinylcarbazole and N-vinyl-3-nitrocarbazole were heated in benzene for 3 hours at 60° C. with aluminum chloride as a catalyzer. The resulting copolymer shows the same sensitivity as in the Example 9.

Example 11

3 g. of 9-vinylanthracene and 1 g. of 2-vinyl-9,10-anthraquinone was copolymerized in a sealed tube employing benzoyl peroxide as an initiator. 1 g. of the resulting copolymer and 0.3 g. of diphenyl chloride were dissolved in 10 cc. of chlorobenzene. The solution obtained was applied to a paper. The coated paper was exposed according to a conventional procedure for 3 seconds employing a mercury lamp as light source. A clear image was produced.

Example 12

5 g. of nitrostyrene and 2 g. of N-vinyl-3-aminocarbazole were heated in benzene for 3 hours at 45° C. with aluminum chloride as a catalyzer. The copolymer thus obtained was dissolved in chlorobenzene and applied to an aluminum plate to produce a layer of 3μ thickness after

drying. The coated plate was subjected to negative charging by a corona discharge according to a conventional procedure, and was exposed for 5 seconds to light from a 100 w. incandescent lamp which was placed 20 cm. away. Thus an image having fidelity to the original was produced.

Example 13

3 g. of N-vinylcarbazole and 1 g. of 1-vinyl-3-nitronaphthalene were heated in benzene for 30 hours employing 0.1 g. of azo-bis-isobutyronitrile at 65° C. 2 g. of the resulting copolymer and 0.8 g. of methyl naphthalene were dissolved in 15 cc. of chlorobenzene. The solution obtained was applied to a paper to produce a layer of 3μ thickness after drying. The coated paper was subjected to a negative charging according to a conventional procedure, by a corona discharge apparatus adjusted to 6 kv. and was exposed for 1.5 seconds to light from a 100 w. incandescent lamp which was placed 20 cm. apart while being superposed with a positive original. A latent image thus produced was developed by applying a developing powder. Thus an image having fidelity to the original, high resolution and excellent contrast was produced. The image was fixed by applying heat.

What we claim is:

1. An electrophotographic material comprising an electrically conducting support having coated thereon a photoconductive layer containing as the photoconductive substance thereof, a photoconductor comprising an organic polymer compound consisting of (1) a vinyl monomer unit carrying an aromatic and/or heterocyclic substituent capable of being an electron donor, and (2) a vinyl monomer unit carrying an aromatic and/or heterocyclic substituent capable of being an electron acceptor, said substituents being capable of combining to form an intramolecular charge transfer complex.

2. An electrophotographic material defined in claim **1**, wherein said vinyl monomer unit (1) is selected from the group consisting of acenaphthylene and its derivatives having an electron donating substituent, N-vinylcarbazole and its derivatives having an electron donating substituent, 1- vinylnaphthalene, 2-vinylnaphthalene and 9-vinylanthracene, and said vinyl monomer unit (2) is selected from the group consisting of 4-nitrostyrene, acenaphthylene derivatives having an electron accepting substituent, N-vinyl-3-nitrocarbazole, 1-vinyl-3-nitronaphthalene and vinylanthraquinone.

3. An electrophotographic material defined in claim **1**, wherein said vinyl monomer unit (1) is 5-nitroacenaphthylene, and said vinyl monomer unit (2) is selected from the group consisting of acenaphthylene, 5-aminoacenaphthylene, and 5-N,N-dimethylaminoacenaphthylene.

4. An electrophotographic material defined in claim **1**, wherein said vinyl monomer unit (1) is N-vinylcarbazole and said vinyl monomer unit (2) is selected from the group consisting of acenaphthylene, 5-nitroacenaphthylene, N-vinyl-3-nitrocarbazole and 1-vinyl-3-nitronaphthalene.

5. An electrophotographic material defined in claim **1**, wherein said vinyl monomer unit (1) is N-vinyl-3-aminocarbazole and said vinyl monomer unit (2) is 4-nitrostyrene.

6. An electrophotographic material defined in claim **1**, wherein said organic polymer compound consists of 55 to 95 mole percent of acenaphthylene as said vinyl monomer unit (1) and 5 to 45 mole percent of 5-nitroacenaphthylene as said vinyl monomer unit (2).

7. An electrophotographic material defined in claim **1**, wherein said organic polymer compound consists of 10 to 80 mole percent of 5-aminoacenaphthylene as said vinyl monomer unit (1) and 20 to 90 mole percent of 5-nitroacenaphthylene as said vinyl monomer unit (2).

8. An electrophotographic material defined in claim **1**, wherein said organic polymer compound consists of 20 to 80 mole percent of N-vinylcarbazole as said vinyl monomer unit (1) and 20 to 80 mole percent of 5-nitroacenaphthylene as said vinyl monomer unit (2).

9. An electrophotographic material according to claim **1** wherein said photoconductive layer further contains a dyestuff sensitizer.

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