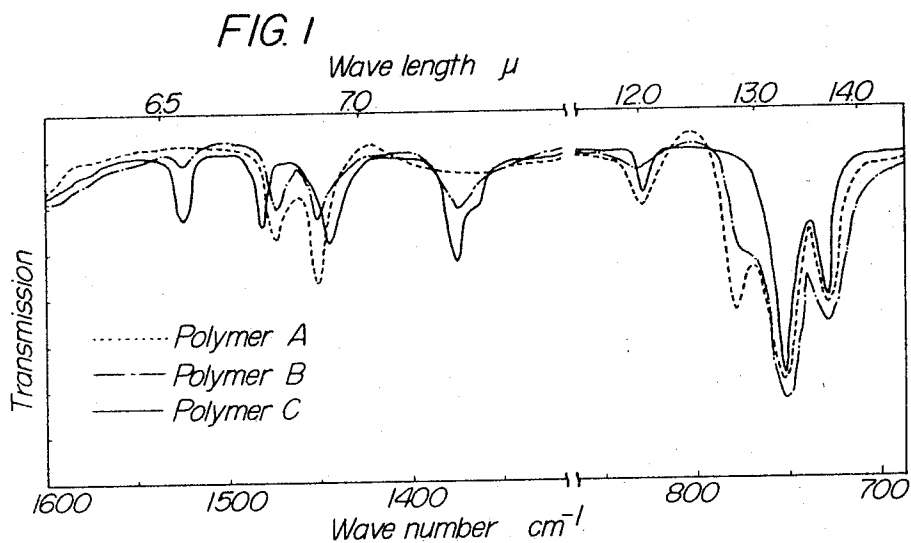
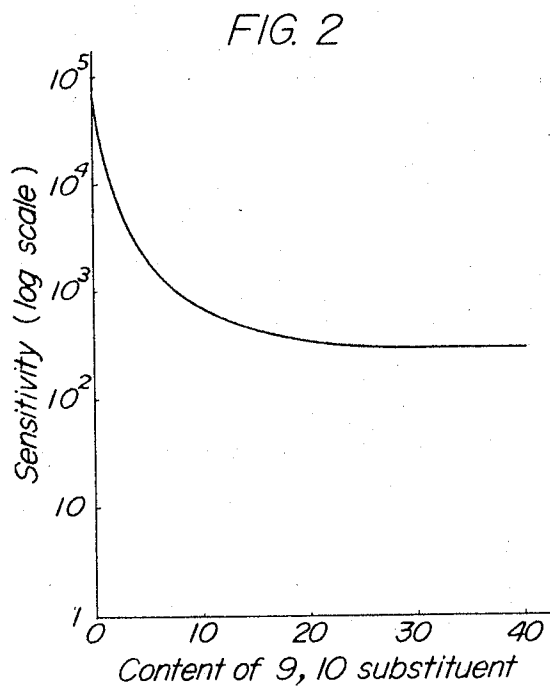


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ELECTROPHOTOGRAPHIC MATERIAL

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3,464,819

ELECTROPHOTOGRAPHIC MATERIAL

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U.S. Cl. 96—1.5

6 Claims

ABSTRACT OF THE DISCLOSURE

An improved highly sensitive photosensitive material for use in electrophotography is composed of a linear polyvinyl anthracene in which anthracene units are included in the chain.

The present invention relates to compositions of the photosensitive materials to be used for electrophotography.

The electrophotography is a reproduction process in which electrostatic phenomenon is utilized in combination with photoconductive phenomena of substance.

The conventional silver-salt photography, although it is excellent in sensitivity, resolution and quality of image, has some disadvantages in that there cannot be obtained high-speed processing and good controlling in processing procedures chiefly because it adopts a chemical and wet-type system, so that it cannot respond to the request of high-speed recording in the present stage. The electrophotography is to eliminate these disadvantages and operates electrically and by dry-type system. There are two examples of this process practiced today, i.e. a process known as Xerography employing selenium photosensitive plate and a process known as Electrofax employing resinous dispersion of zinc oxide. There are other photoconductive materials which can be used in electrophotography. Known examples of inorganic photoconductors are zinc sulfide, cadmium sulfide and others, and examples of organic photoconductors are anthracene, anthraquinone, carbazole and others which are well known from long before. Of late there have been set forth a series of heterocyclic compounds (U.S. Patents Nos. 3,041,165, June 26, 1962; 3,066,023, Nov. 27, 1962) and poly-N-vinyl carbazole mixture (U.S. Patent No. 3,037,861, June 15, 1962) from Kalle Aktiengesellschaft in Germany.

These materials, however, do not satisfy adequately all requirements such as possibility of application, reliability in use, stability, easy handling and high sensitivity. Moreover, they cannot be satisfactory to be modern reproduction material which is to be applied in various fields.

The present invention comprising employing novel organic photoconductive materials which can be used in said electrophotography presents photosensitive materials which have much superior sensitivity and stability as compared with the conventional organic and inorganic photoconductive materials.

Using polyvinylanthracene as electrophotographic material is disclosed in British Patent 941,069 but polyvinylanthracene has extremely poor sensitivity, as stated hereinafter, and so can hardly be used practically.

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The present invention is characterized in that it employs either conversion product of polyvinylanthracene, or polymer obtained by polymerization and conversion of vinylanthracene in the presence of Friedel-Crafts' type catalyst and under a controlled polymerizing condition. Such products (photoconductive materials in the present invention) are divided into two classes depending on methods of preparation; one is soluble into solvent and another is not. Both exhibit extremely high sensitivity when used as electrophotographic material.

The synthesizing methods of 1-vinylanthracene, 2-vinylanthracene and 9-vinylanthracene are well known, see for instance, Journal of Chemical Society, vol. 1957, pages 3858-3862 (by E. G. E. Hawkins).

The following are detailed descriptions illustrating the methods of preparation of the polymers stated herein.

(1) POLYMER A

It is well known that 9-vinylanthracene is possible of cationic polymerization and radical polymerization; for example, dissolving 10 g. of 9-vinylanthracene into 100 ml. of dry toluene, adding thereto 2 mol percent of titanium tetrachloride based on the amount of 9-vinylanthracene, then poly-9-vinylanthracene is obtained in 99% yield. This polymer has a molecular weight of 2400 and melting point of 210° C. to 220° C., and is soluble to benzene, methyl ethyl ketone, tetrahydrofuran and methylene chloride. Polymers of the similar characteristics can also be obtained by cationic polymerization of said material at -78° C. to -10° C. in the presence of Friedel-Crafts' type catalyst such as boron trifluoride, aluminium chloride anhydride or stannic chloride anhydride.

The similar polymer can also be prepared by radical polymerization, employing benzoyl peroxide and di-tert-butyl peroxide. For example, in an ampoule 29 mg. of di-tert-butyl peroxide is added to 4 g. of 9-vinylanthracene, and then the ampoule is flushed with nitrogen gas after it is cooled to -70° C., then it is sealed after reducing pressure and is left for 72 hours for polymerization reaction at 140° C. The product is reprecipitated from benzene-ethanol to obtain light yellow polymer in 64% yield.

Furthermore, the similar polymer may also be made by another process: i.e. 10 g. of refined 9-vinylanthracene is dissolved into 30 ml. of toluene, 2 mol percent of Friedel-Crafts' type catalyst (such as boron trifluoride, sulfuric acid, aluminium chloride anhydride, stannic chloride anhydride, titanium tetrachloride etc.) is added thereto and the mixture is placed in an ampoule and the ampoule is flushed with nitrogen gas and sealed after reducing pressure and then it is left for 24 hours for reaction at -70° C.

The product is reprecipitated from benzene-ethanol to obtain benzene soluble light yellow polymer in 76-93% yield.

The products obtained as stated above are referred to herein as polymer A.

(2) POLYMER B

(a) 10 g. of 9-vinylanthracene is dissolved into 50 ml. of dry benzene. 2 mol percent of titanium tetrachloride based on the amount of 9-vinylanthracene is added thereto. The mixture is then left for two hours for reaction at -70° C. and is heated thereafter gradually to room temperature over a period of one hour. Yellow polymer is obtained in 90-95% yield which is soluble to ben-

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zene and tetrahydrofuran. The similar polymer may also be obtained by cationic polymerization in the presence of Friedel-Crafts' type catalyst such as boron trifluoride, aluminium chloride anhydride or stannic chloride anhydride. The yield is 40-95% in this case.

(b) Furthermore, the similar polymer may also be prepared by the following process: 20 g. of polymer A is dissolved into 100 ml. of benzene, and 0.5-2 mol percent of titanium tetrachloride based on the amount of polymer A is added thereto. The mixture is placed in an ampoule which is sealed after reducing pressure and then left for 0.5-4 hours for reaction at temperature of 5°-20° C. The reaction mixture then is poured into alcohol according to the conventional method to obtain precipitated polymer in 90-98% yield. Friedel-Crafts' type catalyst may be used effectively in the above reaction.

The polymer obtained by method (2) as stated above is referred to herein as "polymer B."

In this case the aimed reaction product could not be obtained at a temperature below 5° C., and the polymer was insolubilized by either reaction at a temperature above 20° C. or reaction for more than four hours.

(3) POLYMER C

(a) 10 g. of 9-vinylanthracene is dissolved into 50 ml. of dry benzene, and 2 mol percent of titanium tetrachloride is added thereto based on the amount of 9-vinylanthracene. Then the mixture is reacted for 24 hours at a temperature of 20°-70° C. Light brown polymer insoluble to solvents is obtained in 90-99% yield.

(b) The similar polymer may also be prepared by cationic polymerization at a temperature of 20°-70° C., employing Friedel-Crafts' type catalyst such as boron trifluoride, aluminium chloride anhydride or stannic chloride anhydride. The yield is 90-99% in this case.

(c) The similar polymer may also be obtained by the following process: 3 g. of refined 9-vinylanthracene is dissolved into 10 cc. of benzene, and thereto is added 0.1 ml. of 10% solution of titanium tetrafluoride in n-hexane. Leaving the reaction mixture for 80 hours at room temperature and under normal pressure, poly-9-vinylanthracene is obtained in the almost stoichiometric yield. The product is insoluble to solvents. This polymer is washed with diluted hydrochloric acid, water and then alcohol to obtain light yellow powder, which is then dried enough.

(d) The similar polymer may also be prepared according to the following process: 20 g. of polymer A is dissolved into 50 ml. of benzene, and 0.5-3 mol percent of Friedel-Crafts' type catalyst, for example titanium tetrachloride is added thereto and the mixture is reacted for 24 hours at a temperature of 20°-70° C. The polymer is obtained in 90-99% yield.

(e) The similar polymer may also be prepared according to the following process; Polymer A is dissolved into methylene chloride and then treated with excess amount of trifluoroacetic acid to form precipitate. The yield is 99%.

(f) Furthermore, the similar polymer may also be obtained by another process as follows; 20 g. of a polymer A is dissolved into 100 ml. of benzene and thereto is added 2 mol percent of Friedel-Crafts' type catalyst such as titanium tetrachloride, aluminium chloride anhydride, stannic chloride anhydride or boron trifluoride. The mixture is reacted at 25° C. in a sealed ampoule under a reduced pressure. The viscosity will increase gradually, then precipitate begin to be formed 1-2 hours after and finally it will be solidified. After leaving it for 24 hours, it is poured into alcohol-hydrochloric acid, washed enough with alcohol and water and then dried. It is washed again with benzene to remove a benzene-soluble product and dried to obtain yellow polymer in 96-99% yield.

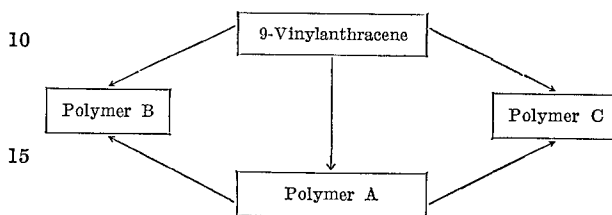
In any reaction processes disclosed above, from (a) to (f), the speed of reaction is so slow at a temperature

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below 20° C. that there cannot obtain the aimed reaction product. And at a temperature above 70° C. the reaction product is colored considerably and its sensitivity is decreased.

The polymer prepared by the methods (a) to (b) as disclosed above is referred to herein as "polymer C."

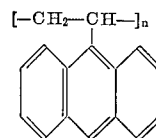
The relation among polymer A, B and C described herein above is shown as follows;



in which arrows show flow of preparation.

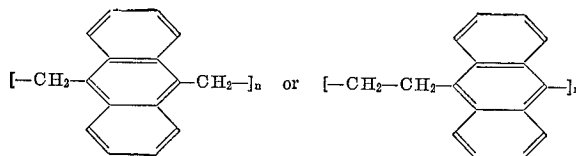
The differences in view of chemical structure among polymers A, B and C obtained according to the processes disclosed above are as follows;

Polymer A, which may be designated as poly-9-vinylanthracene, is a linear polymer represented by the following formula;



and characteristically has infra-red absorption bands at 12.85 μ and 13.25 μ , which means that is attributed to 9-alkyl substituted anthracene.

Polymer C has a structure represented by the following formula;



which has a strong absorption band of infra-red spectrum at 13.25 μ but has not at 12.85 μ . From such an infra-red spectrum, it is clear that the polymer C is poly-9,10-dimethylenanthracene.

Polymer B has a mixed structure of polymer A and polymer C from an infra-red spectrum as shown in FIG. 1. The proportion of the above-mentioned can be calculated from the ratio of the strength of infra-red absorption at 12.85 μ /13.25 μ . The result of the calculation shows that 5-40% of polymer B is composed of polymer C structure units.

Infra-red spectrum of each polymer is shown in FIG. 1.

The present invention comprises employing polymer B or polymer C, whereby such high sensitivity can be obtained that photosensitivity material employing polymer A (poly-9-vinylanthracene) is not in the least comparable therewith.

TABLE 1

Sample:	Sensitivity
Polymer A -----	47,000
Polymer A (sensitized) -----	3,300
Polymer B -----	300
Polymer B (sensitized) -----	70
Polymer C -----	7
Polymer C (sensitized) -----	2-3
Zinc Oxide -----	280
Zinc Oxide (sensitized) -----	12-30
Selenium -----	7

The measuring method for sensitivity reported in Table 1 is described in Bulletin of the Chemical Society of Japan, vol. 37, No. 6, pages 842-844 (by A. Inami et al.) Table 1 illustrates the comparison of sensitivities of the

photo-sensitive material according to the present invention, zinc oxide and selenium photosensitive plate available commercially.

FIG. 2 illustrates the relation between the amount of 9,10-dimethylenanthracene constituent in polymer B and the sensitivity (no sensitizer) of it. It will be seen from this figure that an amount below 5% decreases the sensitivity so much that the polymer cannot be used practically, and an amount above 40% makes the polymer insoluble.

The different solubilities between polymer B and polymer C makes it necessary to change treating in use as a matter of course, which gives various characteristics in each case.

The remarkable characteristic of polymer B is being soluble to solvents. Photosensitive plate is easily prepared by dissolving this polymer into solvent and coating it on supporting material, and coating on transparent supporting material produces transparent photosensitive plate. Another characteristic of this polymer is that it can be sensitized still more by proper sensitizer as well as it has satisfactory sensitivity in itself. In addition it is also possible to increase the strength and flexibility of the photosensitive coat comprising polymer B by employing proper additives.

Examples of effective sensitizers are those which are known as electron-attracting compounds in general, such as tetracyanoethylene, tetracyanoquinodimethane, bromanil, chloranil, benzoquinone, naphthoquinone, anthraquinone, anthraquinone derivatives and Lewis' acids, and such sensitizing dyes as crystal violet, rhodamine, rhodamine B extra, rhodamine 6 G, rose bengal and methyl violet. The proportion of such sensitizer to the polymer may be 1-20% in the case of chemical sensitizers and 0.01-1% in the case of dyestuff sensitizers.

Examples of effective additives are chlorinated paraffin, chlorinated diphenyl, polyvinyl cinnamate, polyvinyl hydrocinnamate, and polyvinyl benzoate. The proportion of such additives to the polymer may be 50-200%.

Referring to the supporting material, there can be used metal plate such as aluminium, zinc and silver; paper subjected to surface treatment with synthetic resin or the like in order that the coating material may not permeate into it; film of synthetic resin which electric resistance is either reduced by treating with antistatic agent or in the order lower by 2 or 3 in itself than the layer of photoconductive material; film of synthetic resin or glass which surface is vacuum-evaporated with metal or copper iodide. The coating may be carried out according to dipping method, flowing method, spraying method, or whirler method.

Polymer C is insoluble into solvents and thus the photosensitive layer comprising this polymer may be in the form of dispersion of polymer C into resin. Examples of resins which can be used as the binder are polystyrene, polyvinyl chloride, polyvinyl chloride copolymer, polyvinyl butyral, polyvinyl acetate, phenolic resin, rosin and dammer resin, the amount of resin employed being 10-500 parts, preferably 50-80 parts per 100 parts of polymer C. This polymer can also be sensitized by certain proper sensitizers in the same manner as in polymer B. And the similar supporting materials and coating methods as in polymer B can be used here.

Any conventional processes may be applied to produce electrophotographic image on the sensitive layers employing the photosensitive materials according to the present invention. The sensitive layer may be charged either positively or negatively but high sensitivity can be obtained by positive charging.

The present invention will further be illustrated by the following examples:

Example 1

1 g. of polymer B and 0.5 g. of chlorinated diphenyl are dissolved into 15 ml. of benzene, coated on an aluminum plate by means of whirler coating and dried to form

a layer of 3μ in thickness. After it is charged positively by means of corona discharge in the conventional manner, it is placed under a positive original and exposed for one second to a 100 w. tungsten lamp at an illumination of 1500 luxes. Then developing powder is scattered thereover to obtain visible image of high fidelity to the original and of high contrast, which can be then fixed with mild heat.

Example 2

1 g. of polymer B, 0.5 g. of chlorinated diphenyl and 0.1 g. of 2-methylantraquinone are dissolved into 15 ml. of chlorobenzene, coated on an aluminum plate by means of whirler coating and dried to form a layer of 3μ in thickness. After it is charged positively by means of corona discharge in the conventional manner, it is placed under a positive original and exposed for one second to the light of 1000 luxes in illumination. Visible image of high fidelity to the original is produced by scattering developing powder over the surface of the plate. The image can be fixed by mild heating.

Example 3

1 g. of polymer B, 0.5 g. of polyvinyl cinnamate, 0.1 g. of 2-methylantraquinone and 0.5 mg. of crystal violet are dissolved into 4 ml. of chlorobenzene, coated on a paper sheet which is in advance subjected to the surface treatment by means of flowing method and dried to form a sensitive layer of 8μ in thickness. This sensitive paper sheet is illuminated for one second by the light of 600 luxes in illumination by means of reflexion method. Visible image of high fidelity to the original is obtained by scattering developing powder.

Example 4

The similar solution as in Example 3 is coated on a polyester film sheet which surface is in advance vacuum-evaporated with copper iodide and then dried to form a sensitive layer of 10μ in thickness. It is exposed through a positive original for one second to the light of 600 luxes in illumination. Visible image of high fidelity to the original is obtained by scattering developing powder.

Example 5

1 g. of fine powdered polymer C is dispersed into a solution in which 1 g. of polyvinyl butyral is dissolved into 5 ml. of benzyl alcohol. The dispersion is coated on an aluminum plate by means of blade and then dried to form a sensitive layer of 7μ in thickness. The sensitive layer is then charged positively with a corona discharger adjusted at about 6 kw., exposed for one second through a positive original to the light of 50 luxes in illumination. Visible image of high fidelity to the original is obtained by scattering developing powder.

Example 6

0.3 g. of polyvinyl butyral, 0.1 g. of 1,2-benzanthraquinone and 0.5 mg. of methylene blue are dissolved into 5 ml. of benzyl alcohol. 1 g. of polymer C is added to the solution and mixed enough. The dispersion is coated by means of blade on a paper sheet which is treated for solvents not to permeate into, and then dried to form a layer of about 7μ in thickness. After it is charged positively with a corona discharger adjusted at about 6 kv., it is exposed for one second by means of reflexion method to the light of 3 luxes in illumination. Visible image of high fidelity to the original is obtained, which may be then fixed by mild heating.

Example 7

0.25 g. of polystyrene, 0.5 mg. of phthalic anhydride and 0.1 g. of 2-methylantraquinone are dissolved into 5 ml. of benzene. 1 g. of polymer C is added to the solution and mixed enough. The dispersion is coated by means of blade on a paper sheet which is treated in advance for solvents not to permeate into, and then dried to form a layer of about 7μ . The sensitive layer is exposed for one

second to the light of 3 luxes in illumination according to the conventional process to obtain visible image of high fidelity to the original.

Example 8

5 g. of fine powder of polymer C and 5 g. of butyral resin are mixed enough in 10 ml. of benzene, coated on an aluminum plate by means of the flowing method and then dried to form a coat of 7μ in thickness. After the coat is charged negatively according to the conventional process with a corona discharger, it is exposed for two seconds through a positive original to the light of 100 luxes in illumination. Scattering developing powder over the surface of it produces visible image of high fidelity to the original, which may be then fixed by mild heating.

Example 9

5 g. of fine powder of polymer C is mixed enough with 3 g. of butyral resin, 1 g. of 2-methylantraquinone and 50 mg. of crystal violet in 20 ml. of ethanol. The mixture is then coated on a paper sheet which is subjected in advance to the surface treatment. The coat is dried to obtain a uniform sensitive layer of 5μ in thickness. Light image of an original is projected onto the paper sheet by means of reflexion method. The exposure time is 0.7 second with the intensity of illumination controlled to be 10 luxes at the white area. Scattering developing powder over the surface of it produces visible image of high fidelity to the original, which can be then fixed with heat.

Example 10

5 g. of polymer C is mixed enough with 5 g. of butyral resin in 10 ml. of benzene, and the mixture is coated on an aluminum plate by means of flowing method and then dried to form a coat of 7μ in thickness. After the coat is charged positively according to the conventional process with a corona discharger adjusted at about 6 kv., it is exposed for one second through a positive original to the light of 10 luxes in illumination. Visible image of high fidelity to the original is obtained by scattering developing powder over the surface of it. The image is then fixed with mild heat.

Example 11

0.5 g. of polymer C, 0.3 g. of 2-methylantraquinone, 50 mg. of crystal violet and 3 g. of butyral resin are mixed enough in 20 ml. of benzyl alcohol and coated on a paper sheet, which is subjected in advance to the surface treatment, to produce a uniform sensitive paper sheet with a dry sensitive coat of 5μ . Light image of an original is projected over the paper sheet by means of reflexion method. Exposure time is 0.4 second with the intensity of illumination of 10 luxes at white area. Scattering developing powder over the surface produces visible image of high fidelity to the original, which can be then fixed with heat.

It is clear from the description disclosed above that the

present invention comprises employing either the conversion product of poly-9-vinylanthracene, or the polymer prepared by polymerization and conversion of 9-vinylanthracene under a controlled polymerization condition in the presence of Friedel-Crafts' type catalyst, and presents photosensitive materials which have quite superior photosensitivity to the conventional organic and inorganic materials for electrophotography, and which is satisfactory for quite various uses including electrophotography.

What we claim is:

1. An electrophotographic material comprising an electrically conducting support having coated thereon a photosensitive material comprising, as a photoconductor thereof, a linear poly-9-vinylanthracene polymer containing at least 5% monomeric units of 9,10-dimethyleneanthracene constituent.

2. An electrophotographic material according to claim 1 wherein said photoconductor is poly-9,10-dimethyleneanthracene converted from 9-vinylanthracene in the presence of a Friedel-Crafts' catalyst.

3. An electrophotographic material according to claim 1 wherein the photosensitive material contains a sensitizer selected from the group consisting of 2-methylantraquinone, 1,2-benzantraquinone, bromanil and tetracyanoquinodimethane.

4. An electrophotographic material according to claim 1 wherein said photoconductor is a linear poly-9-vinylanthracene polymer containing 5-40 percent of 9,10-dimethyleneanthracene constituent converted from 9-vinylanthracene in the presence of a Friedel-Crafts' catalyst.

5. An electrophotographic material according to claim 4 wherein the photosensitive material contains, as a plasticizer, an additive selected from the group consisting of chlorinated diphenyl, polyvinyl cinnamate and polyvinyl benzoate.

6. An electrophotographic material comprising an electrically conducting support having coated thereon a photosensitive material comprising as the photoconductor thereof, a linear poly-9-vinylanthracene polymer containing at least 5% monomeric units of 9,10-dimethyleneanthracene constituent, said polymer being converted from a member selected from the group consisting of 9-vinylanthracene and poly-9-vinylanthracene in the presence of a Friedel-Crafts' catalyst.

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