

United States Patent

Ono et al.

[15] 3,647,428

[45] Mar. 7, 1972

[54] PHOTOCONDUCTIVE MATERIAL FOR ELECTROPHOTOGRAPHY

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[22] Filed: Nov. 27, 1970

[21] Appl. No.: 93,387

[30] Foreign Application Priority Data

Nov. 28, 1969 Japan.....44/95990

[52] U.S. Cl. 96/1.5, 260/85.5 R, 260/85.5 B, 260/86.1 N, 260/47 UA, 117/201, 117/211, 117/161 UN, 252/501, 96/1.6

[51] Int. Cl. G03g 5/06

[58] Field of Search 96/1.5; 260/85.5 R, 85.5 B, 260/86.1 N, 47 UA

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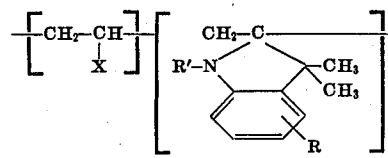
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[57] ABSTRACT

A photoconductive material comprising an electroconductive support having coated thereon a layer containing a sensitizer, a plasticizer and a high-molecular compound having the following repeating unit:



wherein X is CN or COOR', R is hydrogen atom, halogen atom, OR' or COOR' and R' is an alkyl group having one to four carbon atoms.

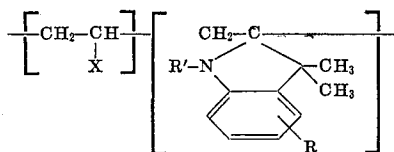
3 Claims, No Drawings

PHOTOCONDUCTIVE MATERIAL FOR ELECTROPHOTOGRAPHY

This invention relates to a photoconductive material for electrophotography. As photoconductive substances useful for electrophotography, there have heretofore been known such inorganic compounds as selenium and zinc oxide, such low molecular organic compounds as anthracene, chrysene and benzidine and such high molecular compounds as poly-N-vinylcarbazole, polyvinylanthracene and polyvinylanthracene.

An object of the present invention is to provide organic photoconductive materials for electrophotography having novel structure, which is entirely different from such heretofore known compounds.

The organic photoconductive materials for electrophotography according to this invention are high molecular compounds having the following repeating units.



(wherein X represents CN or COOR', R represents hydrogen atom, a halogen atom, CR' or COOR', and R' represents a lower alkyl group such as methyl, ethyl, propyl, or butyl).

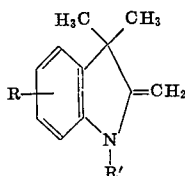
In case where any of the aforementioned compounds is used as a photoconductive material for electrophotography, it is dissolved in a suitable solvent such as tetrahydrofuran, acetone, toluene or benzene and then is casted or coated on an electroconductive base so as to form a photosensitive layer. In this case, by adding a plasticizer and a sensitizer to the solution, the properties of the photosensitive layer can be improved and, at the same time, the sensitivity thereof can be greatly enhanced.

High molecular compounds for the present invention can be obtained by mixing 1-alkyl-2-methylene-3,3-dimethylindoline derivatives with electron-acceptive olefines such as acrylonitrile and acrylestes at desired ratios, adding to the resultant mixtures such radical polymerization initiators as azo-bis-isobutyronitrile and then heating the reactants in a current of nitrogen or in a degassed system.

To cite a concrete example of synthesis, 42 g. of 1,3,3-trimethyl-2-methylenindoline, 26 g. of acrylonitrile and 0.1 g. of azo-bis-isobutyronitrile are placed in a 100-ml. three-neck flask and, while under supply of nitrogen gas and simultaneous agitation, allowed to react for 3 hours at 85° C. The viscosity of reaction solution is increased and becomes glutinous. When this is poured into 2 liters of methanol being vigorously agitated, the polymer settles down while the unreacted monomer is dissolved in the methanol. Through subsequent filtration and drying, there is obtained 21 g. of polymer. The intrinsic viscosity of polymer is 0.175 in tetrahydrofuran at 30° C.

In the similar manner, various copolymers can be obtained by the combinations of monomers as shown in the following table.

Monomer A:



MONOMER B: Electron-acceptive olefin

Monomer A				
Number	Substituent R	Substituent R'	Boiling point	Monomer B
1	H	CH ₃	116.6° C./15 mm. Hg.	CH ₂ =CHCN
2	H	C ₂ H ₅	120° C./10 mm. Hg.	CH ₂ =CHCOOCH ₃
3	Cl	CH ₃	129° C./6 mm. Hg.	CH ₂ =CHCOOCH ₃
4	OCH ₃	CH ₃	132° C./6 mm. Hg.	CH ₂ =CHCOOC ₂ H ₅
5	COOC ₂ H ₅	CH ₃	140° C./4 mm. Hg.	CH ₂ =CHCOOC ₂ H ₅
6	CH ₃	CH ₃	129° C./8 mm. Hg.	CH ₂ =CHCOOC ₄ H ₉

There are metallic plates, papers having an electrophotocductively and plastic films as electroconductive bases providing preferable results.

Useful plasticizers which are used for the purpose of improving film properties include chlorinated paraffins, chlorinated biphenyl, phosphate type plasticizers and phthalate type plasticizers. The amount in which they are added is in the range of 0 to 100 percent by weight based on the aforementioned high molecular compounds.

As sensitizers for increasing the sensitivity, there can be used such known compounds as tetracyanoethylene, tetracyanoquinodimethane, chloranil, bromanil, naphthoquinone, anthraquinone, methylene blue, crystal violet, and malachite green. Desirable results are obtained when such sensitizers are added in the amount not exceeding 10 percent by weight on the total film composition.

It is desirable that the combination of these ingredients, is coated on the electroconductive base in such a thickness that the film on drying has a thickness of 2-20μ. The photosensitive layer consequently obtained is uniformly charged through corona discharge by the usual method, then exposed to light projected through an image, and developed by cascade developing process or liquid developing process to produce a developed image.

Now the present invention is described in more detail by referring to preferred embodiments.

EXAMPLE I

In 100 parts of tetrahydrofuran, there were dissolved 20 parts of 1:2 copolymer ([η] is 0.175 and molecular weight is 41,700) of 1,3,3-trimethyl-2-methyleneindoline and acrylonitrile, 10 parts of chlorinated diphenyl and 1 part of bromanil. The resultant solution was coated on an aluminum plate to a dry thickness of about 5μ. Upon drying of solvent, the layer was charged positively in dark place and, with a film containing a positive image placed thereon, exposed for 1 second to light from a 100-watt tungsten bulb positioned upwardly at a distance of 30 cm., and then treated with a developing agent containing therein a negatively charged toner. Consequently, the positive image was developed. When the layer was placed in the atmosphere to trichloroethylene, there resulted fixing to produce a clear image.

EXAMPLE II

By the same procedure as in Example I, a photosensitive layer was obtained from 1:2 copolymer ([η] is 0.10 and molecular weight is 7,600) of 1,3,3-trimethyl-2-methyleneindoline and ethylacrylate. Through subsequent charging, exposure, developing and fixing, there was obtained a clear image.

EXAMPLE III

By the same procedure as in Example I, a sensitive layer was prepared from 1:5 copolymer ([η] is 0.12) of 1,3,3,5-tetramethyl-2-methyleneindoline and acrylonitrile. Through subsequent charging, exposure, developing, and fixing, there was obtained a clear image.

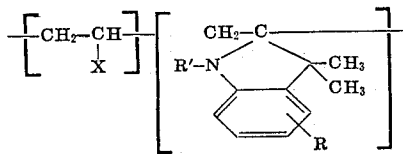
Similar results to those to the examples were obtained by using, in the same procedure, 1:2 copolymer of 1-ethyl-2-methylene-3,3-dimethylindoline and acrylonitrile, 1:5 copolymer of 1,3,3-trimethyl-2-methylene-5-chloroindoline and ethylacrylate, 1:5 copolymer of 1,3,3-trimethyl-2-methylene-5-carboethoxyindoline and acrylonitrile, 1:5 copolymer of 1,3,3-trimethyl-2-methylene-5-methoxyindoline

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and acrylonitrile, 1:2 copolymer of 1,3,3-trimethyl-2-methyleneindoline and methyl-acrylate, and 1:5 copolymer of 1,3,3-trimethyl-2-methyleneindoline and n-butylacrylate.

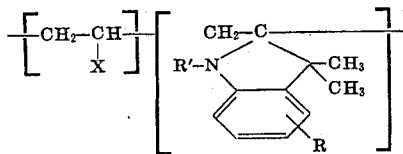
What is claimed is:

1. A photoconductive material comprising an electroconductive support having coated thereon a layer containing a high molecular compound having the following repeating unit:



(wherein X is CN or COOR', R is hydrogen atom, halogen atom, OR' or COOR', and R' is an alkyl group.)

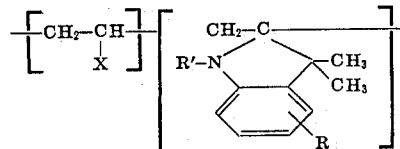
2. A photoconductive material comprising an electroconductive support having coated thereon a layer containing a plasticizer and a high molecular compound having the following repeating unit:



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wherein X is CN or COOR', R is hydrogen atom, halogen atom, OR' or COOR', and R' is an alkyl group having one to four carbon atoms.

3. A photoconductive material comprising an electroconductive support having coated thereon a layer containing a sensitizer, a plasticizer and a high molecular compound having the following repeating unit:



wherein X is CN or COOR', R is hydrogen atom, halogen atom, OR' or COOR', and R' is an alkyl group having one to four carbon atoms.

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