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(54) **An organic photosensitive composition for electrophotography.**

(57) An organic photosensitive composition for electrophotography comprising poly-N-vinylcarbazole as a charge-transfer medium and vinylidene chlorideacrylonitrile copolymer as an additive for improving the mechanical strength of said poly-N-vinylcarbazole.

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AN ORGANIC PHOTOSENSITIVE COMPOSITION FOR ELECTROPHOTOGRAPHY

This invention relates to an organic photosensitive composition for electrophotography which is superior in mechanical strength and which has an enhanced sensitivity.

In order to obtain clear and distinct images, the surface of a photosensitive layer must be uniformly charged with static electricity. For this purpose, it is essential that the photosensitive layer is formed with a smoothness and an even thickness on the surface of a conductive substrate. Such a photosensitive layer is produced by a variety of inorganic or organic photosensitive materials. Inorganic photosensitive materials provide a photosensitive layer the surface of which is hard and excellent in durability, so that they can be preferably used for photosensitive layers to be applied to large-scaled and high-speed copying machines. However, the inorganic photosensitive materials are expensive and some of them are harmful to human beings. Thus, in recent years, organic photosensitive materials are more popular than inorganic photosensitive materials for copying machines, especially low-speed copying machines.

As organic photosensitive materials, poly-N-vinylcarbazole is generally used, but it is brittle so that the resulting photosensitive layer is inferior in abrasion-resistance. Although a conventional organic photosensitive material which contains poly-N-vinylcarbazole and polycarbonate as an additive functioning to improve the abrasion-resistance of the resulting photosensitive material is known, the abrasion-resistance is

still insufficient, so that the organic photosensitive material cannot provide organic photosensitive compositions having excellent durability.

Thus, wear of the photosensitive layer resulting from blade-cleaning and abrasion of the surface of the photosensitive layer resulting from paper-jamming cannot be prevented.

In attempting to increase the mechanical strength of an organic photosensitive material such as poly-N-vinylcarbazole, the inventors of this invention discovered that the use of a gummy resin material as an additive can improve the mechanical strength of poly-N-vinylcarbazole. They finally succeeded in obtaining a novel organic photosensitive material having excellent abrasion-resistance and hardness.

The organic photosensitive composition for electrophotography of this invention, which overcomes the above-discussed and numerous other disadvantages and deficiencies of the prior art, comprises poly-N-vinylcarbazole as a charge-transfer medium and vinylidene chloride-acrylonitrile copolymer as an additive for improving the mechanical strength of said poly-N-vinylcarbazole.

The vinylidene chloride-acrylonitrile copolymer is, in a preferred embodiment, contained in an amount of 5 to 25 parts by weight per 100 parts by weight of poly-N-vinylcarbazole.

The organic photosensitive composition further comprises, in a preferred embodiment, an electron acceptor in an amount of 10 to 40 parts by weight per 100 parts by weight of poly-N-vinylcarbazole and/or an electron donor in an amount of 10 to 60 parts by weight per 100 parts by weight of poly-N-vinylcarbazole.

Thus, the invention described herein makes possible the objects of (1) providing an organic photosensitive composition for electrophotography which is superior in mechanical strength; (2) providing an organic photosensitive composition for electrophotography from which a photosensitive layer having an extremely hard surface can be produced allowing for the minimization of a decrease in the surface potential of the photosensitive layer, resulting in a distinct and clear image; (3) providing an organic photosensitive composition for electrophotography which has an enhanced sensitivity; and (4) an organic photosensitive composition for electrophotography in which the reduction of the surface potential due to repeated light exposure is very much decreased.

This invention provides a novel organic photosensitive layer having extremely superior abrasion-resistance and extremely high surface-hardness, compared with conventional photosensitive layers, notwithstanding that the photosensitive layer is made using vinylidene chloride-acrylonitrile copolymer which is neither hard nor binding. Therefore, resin materials having a high degree of hardness such as polycarbonate need not be used as an additive for improving a mechanical strength of poly-N-vinylcarbazole.

According to this invention, vinylidene chloride-acrylonitrile copolymer is contained in an amount of 5 to 25 parts by weight, preferably 7 to 15 parts by weight, per 100 parts by weight of poly-N-vinylcarbazole. When vinylidene chloride-acrylonitrile copolymer is contained in an amount of less than 5 parts by weight per 100 parts by weight of poly-N-vinylcarbazole, the resulting photosensitive layer has insufficient mechanical strength. When vinylidene chloride-acrylonitrile copolymer is contained in an amount of more than 25 parts by weight per 100 parts by weight of poly-N-vinylcarbazole, the content of poly-N-vinylcarbazole is relatively reduced so that poly-N-vinylcarbazole cannot sufficiently function as a charge-transfer medium.

Vinylidene chloride-acrylonitrile copolymer is synthesized by ordinal radical polymerization using radical polymerization initiators such as peroxides (e.g., benzoyl peroxide), azo-compounds (e.g.,

azobisisobutyronitrile), etc.

For the purpose of an enhancement of the sensitivity of the photosensitive layer and a decrease in the residual potential of the photosensitive layer, known electron acceptors may be incorporated in an amount of 10 to 40 parts by weight, preferably 20 to 35 parts by weight, per 100 parts by weight of poly-N-vinylcarbazole. As these electron acceptors, chloranil, naphthoquinone, phthalic anhydride, nitrofluorenone, etc., can be used.

In order to further improve the sensitivity of the photosensitive layer and decrease the reduction of the surface potential of the photosensitive layer due to the repeated light exposure (i.e., to improve the aging characteristic), known electron donors, for example, phenanthren, diethyl aminophenylbenzaldehyde diphenylhydrazone, ethyl carbazolealdehyde diphenylhydrazone, triphenyl amine, etc., may be incorporated in an amount of 10 to 60 parts by weight, preferably 20 to 50 parts by weight, per 100 parts by weight of poly-N-vinylcarbazole.

A vinylidene chloride-acrylonitrile copolymer synthesized by polymerization is dissolved in an appropriate solvent such as tetrahydrofuran, cyclohexane or the like, together with poly-N-vinylcarbazole and, as desired, an electron acceptor and/or an electron donor. The resulting solution is coated with a certain thickness on a conductive substrate, resulting in an organic photoconductor for electrophotography.

Example

One hundred parts by weight of poly-N-vinylcarbazole (manufactured by Anan Kohryo Co., Japan), 10 parts by weight of vinylidene chloride-acrylonitrile copolymer (Saran resin F-310; a number average molecular weight of 43,000; a weight average molecular weight of 120,000; manufactured by Asahi Dow Co.), 8 parts by weight of N,N'-di(3,5-dimethylphenyl)perylene-3,4,9,10-tetracarboxic acid diimide, 20 parts by weight of 2,3-dichloro-1,4-naphthoquinone, 40 parts by weight of phenanthrene, and 20 parts by weight of tetrahydrofuran were mixed in a stainless ball mill for 24 hours. The mixture was coated on an aluminum plate having a thickness of 80 μm by means of a wire bar and dried at 100°C for 1 hour, resulting in a photoconductor having a photosensitive layer thereon with a thickness of 14 μm. The photosensitive layer had a surface-hardness of 2H, which was determined by comparison with the hardness of pencils according to JIS (the Japanese Industrial Standards) scale of HB, F, H, 2H, ...

The photoconductor was applied to an electrophotographic copying machine DC-191 (supplied by Mita Industrial Co., Ltd.) wherein an electrophotographic process was repeated 4×10^4 times.

The accompanying figure shows the relationship between the aging cycle of the photosensitive layer and the thickness of the photosensitive layer, indicating that wear of the photosensitive layer of this invention was surprisingly minimized even though it was used in a electrophotographic copying machine for a long period of time, compared with a conventional photosensitive layer.

The sensitivity of the photosensitive layer of this invention was 15 lux·second, which is the exposure quantity for half decay of the potential. The smaller the value of the exposure quantity for the half decay of the potential, the higher the sensitivity becomes. Moreover, the surface potentials of the photosensitive layer were 600 V and 550 V at the first and the 500th cycle, respectively. The difference therebetween was only 50 V, indicating that the reduction of the surface potential due to the repeated light exposure was surprisingly decreased (i.e., the aging characteristic is extremely improved). The residual potential of the photosensitive layer, which was 20 V at the first, was largely retained even at the 500th cycle, indicating that the photosensitive layer supplied clear and distinct images over a long period of time.

Control 1

One hundred parts by weight of poly-N-vinylcarbazole (manufactured by Anan Kohryo Co., Japan), 10 parts by weight of polycarbonate (panlight L manufactured by Teijin Co., Japan), 8 parts by weight of N,N'-di(3,5-dimethylphenyl)perylene-3,4,9,10-tetracarboxic acid diimide, 20 parts by weight of 2,3-dichloro-1,4-naphthoquinone, 40 parts by weight of phenanthrene, and 20 parts by weight of tetrahydrofuran were mixed in a stainless ball mill for 24 hours.

A control photoconductor was prepared using the mixture in the same manner as the photoconductor in the above-mentioned example. The surface-hardness of the photosensitive layer of the control photoconductor was determined to be F according to JIS.

The photoconductor was applied to an electrophotographic copying machine in the same manner as in the above-mentioned example. The relationship between the aging cycle of the control photosensitive layer and the thickness of the control photosensitive layer is shown in the accompanying figure, indicating that the thickness of the control photosensitive layer was significantly reduced, while that of the photosensitive layer of this invention was almost unchanged. This means that the photoconductor of this invention is superior in abrasion-resistance and surface-hardness.

Control 2

Ten parts by weight of poly-N-vinylcarbazole (manufactured by Anan Kohryo Co., Japan), 10 parts by weight of polyester (biron 200 manufactured by Toyobo Co., Japan), 8 parts by weight of N,N'-di(3,5-dimethylphenyl)perylene-3,4,9,10-tetracarboxic acid diimide, 20 parts by weight of 2·3-dichloro-1,4-naphthoquinone, 40 parts by weight of phenanthrene, and 20 parts by weight of tetrahydrofuran were mixed in a stainless ball mill for 24 hours.

A control photoconductor was prepared using the mixture in the same manner as in the above-mentioned example. The surface-hardness of the control photosensitive layer was determined to be F according to JIS, which indicates that the surface-hardness of the control photosensitive layer was inferior to that of the photosensitive layer of this invention.

Control 3

Preparation and examination were carried out in the same manner as in the above-mentioned example except that naphthoquinone was not used. The surface-hardness of the photosensitive layer of the resulting

control photoconductor was 2H.

However, the sensitivity of the control photosensitive layer was about 32 lux·second, which contrasts strikingly with that of the photosensitive layer of this invention, 15 lux·second. The surface potential of the control photosensitive layer was 600 V at the first and it was almost unchanged even at the 500th cycle of a charging-discharging (exposure) process, but the residual potential of the control photosensitive layer, which was 100 V at the first, increased to 150 V at the 500th cycle. These values of the residual potential of the control layer are very much higher than that of the photosensitive layer of this invention, as low as 20 V. These facts indicate that the sensitivity of the photosensitive layer of this invention containing an electron acceptor such as naphthoquinone is superior to that of the control layer lacking such an electron acceptor.

Control 4

Preparation and examination were carried out in the same manner as in the above-mentioned example except that phenanthrene was not used. The surface-hardness of the photosensitive layer of the resulting control photoconductor was 2H. The sensitivity of the control photosensitive layer was 17 lux·second. The surface potentials of the control photosensitive layer, which were 600 V at the first, decreased to as low as 300 V at the 500th cycle, which contrasts strikingly with that of the photosensitive layer of this invention mentioned above. Moreover, the residual potential of the photosensitive layer from the first to the 500th cycle was approximately the same value, 40 V, which is somewhat higher than that of the photosensitive layer of this invention, 20V. These

facts mean that the sensitivity of the photosensitive layer of this invention containing an electron donor such as phenanthrene is superior to that of the control layer lacking such an electron donor.

Claims:

1. An organic photosensitive composition for electrophotography comprising poly-N-vinylcarbazole as a charge-transfer medium and vinylidene chloride-acrylonitrile copolymer as an additive for improving the mechanical strength of said poly-N-vinylcarbazole.

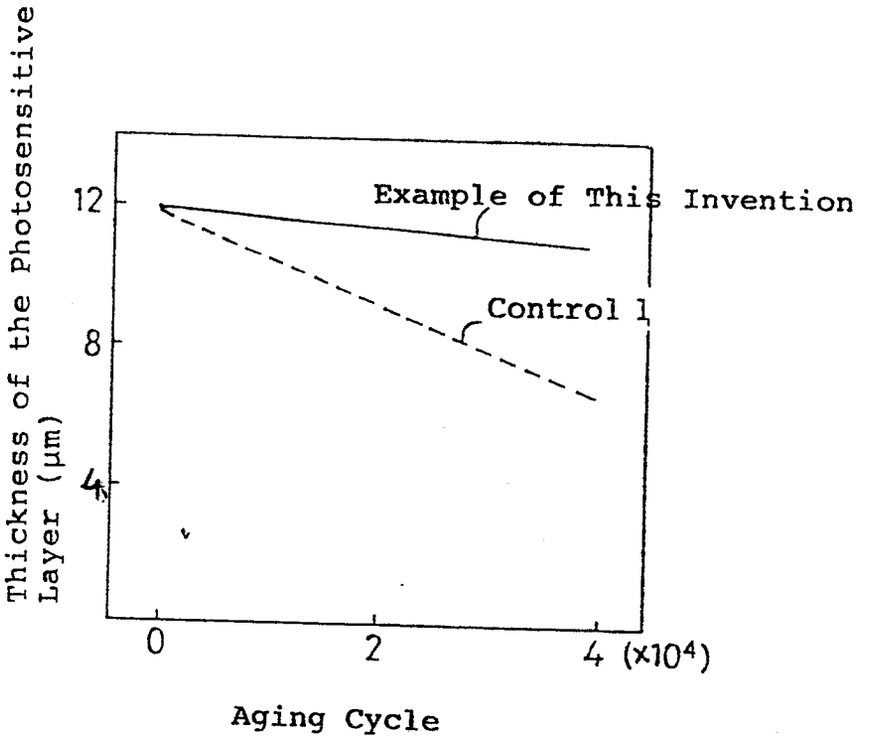
2. An organic photosensitive composition for electrophotography according to claim 1, wherein said vinylidene chloride-acrylonitrile copolymer is contained in an amount of 5 to 25 parts by weight per 100 parts by weight of poly-N-vinylcarbazole.

3. An organic photosensitive composition for electrophotography according to claim 1, which further comprises an electron acceptor.

4. An organic photosensitive composition for electrophotography according to claim 1, 2 or 3, which further comprises an electron donor.

5. An organic photosensitive composition for electrophotography according to claim 3, wherein said electron acceptor is contained in an amount of 10 to 40 parts by weight per 100 parts by weight of poly-N-vinylcarbazole.

6. An organic photosensitive composition for electrophotography according to claim 4 or 5, wherein said electron donor is contained in an amount of 10 to 60 parts by weight per 100 parts by weight of poly-N-vinylcarbazole.


Thickness of the Photosensitive Layer (μm)
12
8
4
0
2
4 (×10⁴)
Example of This Invention
Control 1
Aging Cycle

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 86305899.0

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US - A - 4 160 666 (MC CABE) * Claims 1,3,9,21,30; column 8, lines 38-44; column 9, lines 25,26,31,32 * --	1,4	G 03 G 5/05 G 03 G 5/07
X	US - A - 4 451 548 (KINOSHITA) * Claims 1,5,6,10; column 10, line 32 - column 11, line 14 * --	1,3	
X	US - A - 3 938 994 (REYNOLDS) * Claims 1,3,4,6; column 5, lines 15-28 * --	1,4	
X	DE - A1 - 3 329 054 (CANON) * Claims 1,16; page 50, lines 8-17; page 54, lines 13-17 * --	1	
A	US - A - 4 302 522 (GARNETT) * Claims 1-5 * --	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 03 G
A	US - A - 3 917 482 (FIDA) * Claim 1; column 2, lines 20-30 * ----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	07-11-1986	SCHÄFER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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