United States Patent [19]

Matsumoto et al.

[11] **3,868,251**

[45] **Feb. 25, 1975**

[54] **ORGANIC PHOTOCONDUCTIVE COMPOSITION CONTAINING CHLORINATED PARAFFIN**

[75] Inventors: **Shoichi Matsumoto; Kazuyoshi Saito,** both of Yokohama, Japan

[73] Assignee: **Tokyo Shibaura Electric Co., Ltd.,** Kawasaki-shi, Japan

[22] Filed: **July 23, 1973**

[21] Appl. No.: **381,746**

[30] **Foreign Application Priority Data**

July 28, 1972 Japan 47-75131

[52] **U.S. Cl.** **96/1.5,** 96/1.6

[51] **Int. Cl.** **G03g 5/06**

[58] **Field of Search** ..... 96/1 M, 1 PS, 1.5, 1.6, 96/1.8; 252/501

[56] **References Cited**

UNITED STATES PATENTS

3,287,114	11/1966	Hoegl	96/1.5
3,533,787	10/1970	Merrill et al.	96/1.5
3,652,269	3/1972	Coutois et al.	96/1.5
3,718,463	2/1973	Young	96/1.5 X

FOREIGN PATENTS OR APPLICATIONS

883,783	12/1961	Great Britain	96/1.5
678,953	1/1964	Canada	96/1.5
678,949	1/1964	Canada	96/1.5

Primary Examiner—Roland E. Martin, Jr.
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

An organic photoconductive composition for use in electrophotography containing 20 to 50 parts by weight of chlorinated paraffin with respect to 100 parts by weight of organic photoconductor.

5 Claims, 2 Drawing Figures

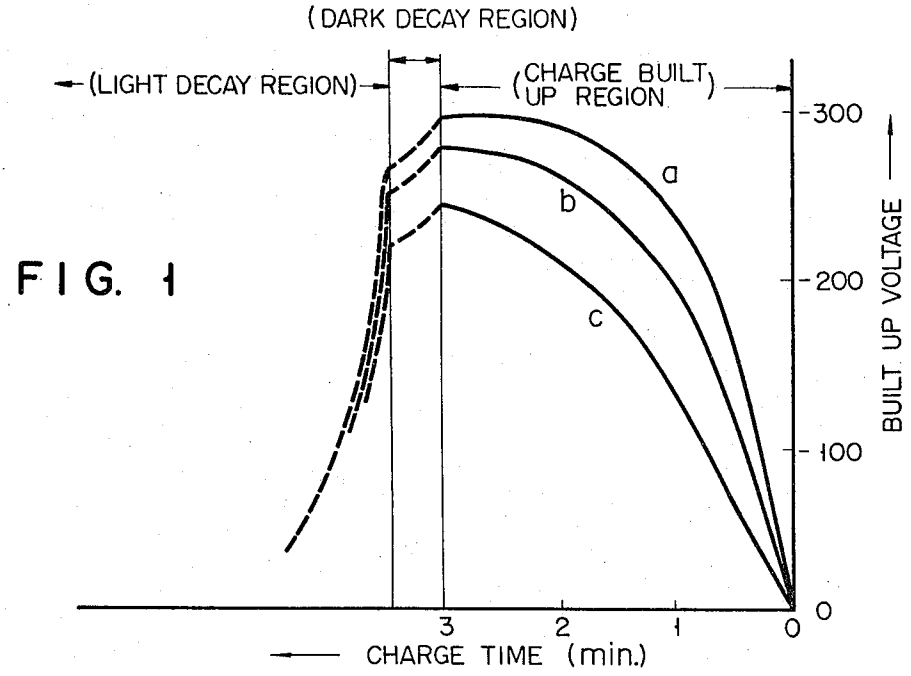
(DARK DECAY REGION)
(LIGHT DECAY REGION)
(CHARGE BUILT UP REGION)
a
b
c
300
200
100
0
BUILT UP VOLTAGE
3
2
1
0
CHARGE TIME (min.)

FIG. 1

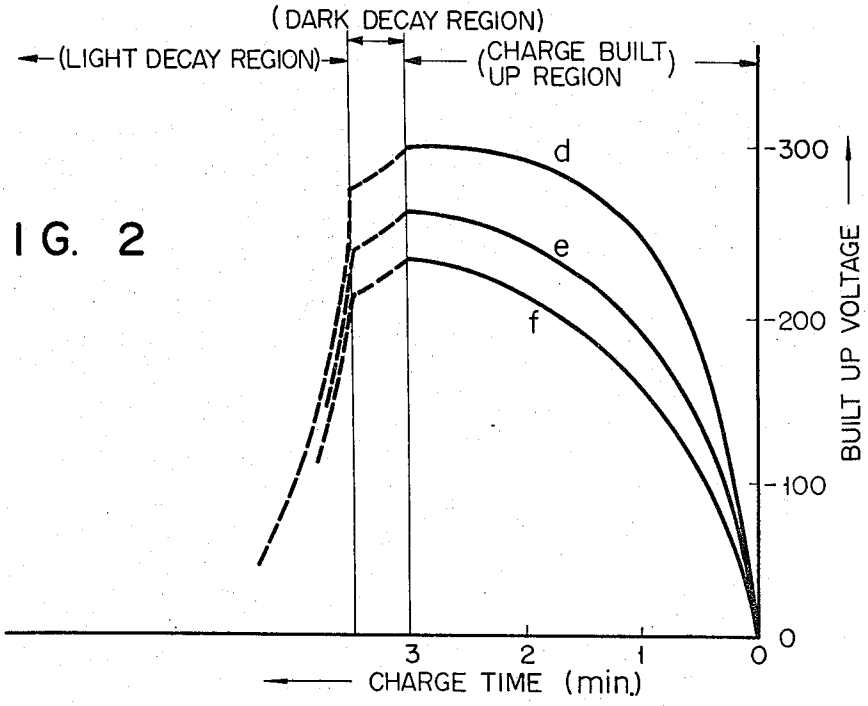
(DARK DECAY REGION)
(LIGHT DECAY REGION)
(CHARGE BUILT UP REGION)
d
e
f
300
200
100
0
BUILT UP VOLTAGE
3
2
1
0
CHARGE TIME (min.)

FIG. 2

ORGANIC PHOTOCONDUCTIVE COMPOSITION CONTAINING CHLORINATED PARAFFIN

This invention relates to an organic photoconductive composition for use in electrophotography, and more particularly to such composition designed for the prevention of deterioration in its characteristics due to electrical charge or light exposure.

An organic photosensitive material for use in electrophotography has been developed which consists essentially of a polymeric organic photoconductor, examples of which include poly-N-vinylcarbazole, charge-transfer molecular complexes such as poly-N-vinylcarbazole-tetrachloro-p-benzoquinone and poly-N-vinylcarbazole-tetracyanoquinodimethane, poly-N-vinylcarbazole derivatives such as nitrated poly-N-vinylcarbazole, polyvinylanthracene, and polyacenaphthylene; and monomeric organic photoconductors such as anthracene, pyrazoline, oxazole, triazole and hydrazone.

This type of organic photosensitive material has many advantages over known inorganic photosensitive material consisting essentially of selenium or zinc oxide, etc. in easy sensitization, transparency, good film formation, high flexibility, light weight, and low manufacturing cost. Hence there is a growing interest in its practical applications.

There are, however, the serious disadvantages in that the photosensitive materials consisting chiefly of the abovementioned organic photoconductors suffer fatigue due to electrical charging or light exposure, especially a marked deterioration in initial built-up voltage and a considerable decrease in saturation potential, thus constituting a fatal obstacle in its practical applications. In more detail, this type of organic photosensitive material is not suitable for its repeated use in such electrophotographic copying, as a toner or a charge transfer copying due to its fatigue failure during repeated use. Even when it is not repeatedly used, for example, it is used as a material of photosensitive paper, it gives rise to an undesired problem, such as a reduction in image density because of the fatigue failure due to roomlight exposure.

Accordingly, it is an object of this invention to provide an organic photoconductive composition for use in electrophotography which can always perform a predetermined function without deterioration in characteristics due to the fatigue caused when used repeatedly in an electrophotographic copying, such as a toner or a charge transfer copying and when used as a photosensitive material for a photosensitive paper.

In accordance with this invention there is provided a photoconductive composition for use in electrophotography comprising 100 parts by weight of an organic photoconductor and 20 to 50 parts by weight of chlorinated paraffin.

FIGS. 1 and 2 show characteristic curves of built-up voltage vs charge time for a photosensitive plate consisting of an organic photoconductor for use in electrophotography to explain the characteristics of the photoconductor.

The organic photoconductive composition of this invention can be prepared by mixing 100 parts by weight of organic photoconductor, about 0.1 to 20 parts by weight of chemical sensitizer, about 0.02 to 4 parts by weight of optical sensitizer and 20 to 50 parts by weight of chlorinated paraffin.

The composition may be dissolved in a suitable solvent such as chlorobenzene, toluene, benzene, methylene chloride or the like and uniformly stirred to form a photosensitive material.

Organic photoconductor which has been found to be suitable for the composition of the invention is, for example, poly-N-vinylcarbazole, charge-transfer molecular complexes such as poly-N-vinylcarbazole-tetrachloro-p-benzoquinone or poly-N-vinylcarbazole-tetracyanoquinodimethane, poly-N-vinylcarzole derivatives such as nitrated poly-N-vinylcarbazole, polyvinylanthracene, polyacenaphthylene, anthracene, pyrazoline, oxazole, triazole, or hydrazone. To increase photosensitivity, a chemical sensitizer and/or an optical sensitizer may be added to these photoconductors. Various kinds of additives may also be added to improve other properties of the photosensitive material. Especially in a monomolecular organic photoconductor, a suitable polymer such as polymethylmethacrylate, polycarbonate, cellulose nitrate or cellulose acetate is preferably added as a binder to provide film formation.

Prefered examples of chlorinated paraffin are Adekacizer-E-410, Adekacizer-E-450, Adekacizer-E-480, Adekacizer-E-500, Adekacizer-E-520 (trade names of chlorinated paraffins manufactured by Adeka-Argus Chemical Co., Ltd., containing 41 to 52% by weight of chlorine); Enpara K-45, Enpara K-50, Enpara K-65 (trade names of chlorinated paraffins produced by Ajinomoto Kabushiki Kaisha, containing 40 to 65% by weight of chlorine); and Monocizer-W-40, Monocizer-W-45, Monocizer-W-50 (trade names of chlorinated paraffins by Dainippon Ink and Chemicals, Inc.)

These chlorinated paraffins contain about eight to 18 carbon atoms, in either liquid or solid state depending on the chlorine content. Taking into account the compatibility with the organic photoconductor, chlorinated paraffin in liquid state containing 40 to 65% by weight of chlorine is most preferred. A mixture of two or more kinds of chlorinated paraffin may also be used.

The amounts of chlorinated paraffin to be mixed with the organic photoconductor should be within the range of 20 to 50 parts by weight against 100 parts by weight of the organic photoconductor. This is because the addition of chlorinated paraffin not exceeding 20 parts by weight cannot prevent the occurrence of fatigue failure or deterioration, while the addition of chlorinated paraffin exceeding 50 parts by weight causes a marked reduction in photosensitivity and a considerable decrease in the built-up voltage, although the occurrence of fatigue failure or deterioration may be prevented effectively. It has been experimentally confirmed that the addition of chlorinated paraffin exceeding the upper and lower limits were unsuitable for practical applications to photoconductors for use in electrophotography.

As described above, the organic photoconductive composition for electrophotography obtained by mixing an organic photoconductor with a predetermined amount of chlorinated paraffin can prevent or suppress the occurrence of fatigue failure or deterioration, thus performing the desired functions in use as a photosensitive material. Although the operating mechanism of chlorinated paraffin is unknown, it has been found that a photosensitive material containing an organic photoconductor as a main component will suffer in practice negligibly little fatigue failure or deterioration due to

electric charge or light exposure by adding chlorinated paraffin. Even when repeatedly used as a photosensitive material for a toner or a charge transfer copying the composition of the invention can always perform a predetermined function as a photosensitive material. Even when applied to a photosensitive paper, it can obtain a clear image without causing a reduction in its image density due to room-light exposure fatigue failure or deterioration.

The organic photoconductive composition of the invention will now be described in detail by following examples. Throughout the examples "parts" means "parts by weight."

EXAMPLE 1

A charge-transfer reaction was carried out between poly-N-vinylcarbazole and tetrachloro-p-benzoquinone in a weight ratio of 1:1.27 to obtain a charge-transfer molecular complex. A mixture of 100 parts of the charge-transfer molecular complex, 0.5 part of 3, 5 dinitrosalicylic acid as a chemical sensitizer and 0.5 part of Brilliant Green as an optical sensitizer was dissolved in 1,800 parts of chlorobenzene. The resultant solution was divided into seven equal parts. Adekacizer-E-410 was added to each part at the rate indicated in Table 1 with respect to 100 parts of the charge-transfer molecular complex. The Adekacizer-E-410 is a trade name of chlorinated paraffin manufactured by Adeka-Argus Chemical Co., Ltd., containing 41% by weight of chlorine. Each solution was coated on aluminium plate substrates to form, when the solution is dried, seven photosensitive plate samples having a film thickness ranging between 5 and 6 μm.

Table 1

Sample No.		Amount of chlorinated paraffin added, parts	Fatigue index (%) due to light exposure of 4000 lux. sec. 1 min.	3 min.
(Control)	1	0	44	21
	2	10	15	13
	3	20	2	3
	4	25	0	1
	5	35	1	0
	6	45	0	2
	7	50	2	0

FIG. 1 shows the results of measuring the electrophotographic characteristic curves of Sample 1 by a paper analyzer (rotation-speed of a sample turntable: 13 rpm; corona charging voltage: −5,000V; light source tungsten-filament lamp; illumination: 9 lux.). The curves (*a*), (*b*) and (*c*) in FIG. 1 indicate the results obtained when light of 0, 1,000 and 4,000 lux.sec., respectively, are irradiated over the surface of the sample prior to measurement. It is clear from FIG. 1 that a sample with no addition of chlorinated paraffin suffered much fatigue (deterioration in initial built-up voltage and reduction in saturation voltage). More exactly, the fatigue index due to light exposure is defined by

$$(V_O - V_L/V_O \times 100\ (\%)$$

where

V_L = built-up voltage of a sample subjected to light exposure of 4,000 lux.sec. prior to measurement, and

V_O = built-up voltage of a sample when subjected to no previous light exposure.

According to this definition, the fatigue indexes of Sample 1 are as follows:

44%—1 minute after the commencement of charging (mainly a deterioration in built-up voltage, as shown clearly in FIG. 1); and

21%—3 minutes after the initiation of charge (chiefly a deterioration in saturation voltage).

Similarly, the fatigue indexes of Samples 2 to 7 due to light exposure were measured. Related results were shown also in Table 1.

It is evident from Table 1 that a photoconductive composition obtained by adding not less than 20 parts of chlorinated paraffin to 100 parts of an organic photoconductor suffers substantially no fatigue failure due to light exposure. Addition of not less than 50 parts of chlorinated paraffin became impractical because of the considerable reduction in both of photosensitivity and initial built-up voltage.

EXAMPLE 2

The process of Example 1 was essentially repeated except that Adakacizer-E-410 was replaced with Adekacizer-E-520 (trade name of chlorinated paraffin manufactured by Adeka-Argus Chemical Co., Ltd., containing 52% by weight of chlorine). Samples 8 to 14 having the compositions shown in Table 2 were thus obtained.

Table 2

Sample No.		Amount of chlorinated paraffin added, parts	Fatigue index (%) due to repeated use: 1 min.	3 min.
(Control)	8	0	29	23
	9	10	18	16
	10	20	3	0
	11	25	2	1
	12	35	0	2
	13	45	1	0
	14	50	0	1

The electrophotographic characteristics of Sample 8 were repeatedly measured by the paper analyzer as in Example 1. Related results were obtained, as indicated in FIG. 2. Note that the curves (*d*), (*e*) and (*f*) in FIG. 2 are the results of the first, second and third successive measurements, respectively. It is clear from FIG. 2 that a sample without addition of chlorinated paraffin suffered heavy fatigue due to its repeated use (mainly due to charging). The fatigue index due to light exposure is defined by

$$(V_O - V_R/V_O) \times 100\ (\%)$$

where

V_O = built-up voltage of a sample at the first measurement, and

V_R = built-up voltage of a sample at the third measurement.

According to this definition, the fatigue indexes of Sample 8 are as follows:

29%—1 minute later; and

23%—3 minutes later.

Similarly, the fatigue indexes of Samples 9 to 14 due to their repeated use were measured. Related results thus obtained are listed in Table 2.

It is obvious from Table 2 that a photosensitive material having not less than 20 parts by weight of chlorinated paraffin suffered substantially no fatigue.

EXAMPLE 3

A mixture of 100 parts of poly-N-vinylcarbazole, 10 parts of 2, 4, 7-trinitrofluorenone (a chemical sensitizer), and 30 parts of Enpara K-45 (trade name of chlorinated paraffin produced by Ajinomoto Kabushiki Kaisha, containing 45% by weight of chlorine) was dissolved in 1,800 parts of tetrahydrofuran to prepare a photosensitive solution. The surface of an aluminium plate support was coated with this solution and then dried to produce a sample of photosensitive plate. The fatigue indexes of the sample due to light exposure were measured as in Example 1. Related results were 2% in 1 min. and 0% in 3 min., whereas the corresponding fatigue indexes in a control experiment with no addition of chlorinated paraffin were 33% (1 min.) and 20% (3 min.).

EXAMPLE 4

The process of Example 3 was substantially repeated except that poly-N-vinylcarbazole was replaced with polyacenaphthylene. The measured fatigue indexes of the sample due to light exposure were 1% 1 minute later and 2% 3 minutes later.

It will be readily understood from the foregoing description that a photoconductive composition for use in electrophotography comprising 100 parts by weight of an organic photoconductor and 20 to 50 parts by weight of chlorinated paraffin will suffer practically no fatigue failure or deterioration due to electric charge or light exposure. Accordingly, the composition of the invention will always display a predetermined function, even when repeatedly used as a photosensitive material in a toner or a charge transfer copying.

What we claim is:

1. A photoconductive composition for use in electrophotography comprising 100 parts by weight of an organic photoconductor and 20 to 50 parts by weight of chlorinated paraffin wherein said chlorinated paraffin contains 40 to 65% by weight of chlorine and wherein said chlorinated paraffin contains eight to 18 carbon atoms.

2. A photoconductive composition for use in electrophotography comprising 100 parts by weight of an organic photoconductor and 20 to 50 parts by weight of chlorinated paraffin wherein said chlorinated paraffin contains 40 to 65% by weight of chlorine and wherein said chlorinated paraffin contains eight to 18 carbon atoms, wherein said organic photoconductor is one member selected from the group consisting of poly-N-vinylcarbazole, charge-transfer molecular complexes, poly-N-vinylcarbazole derivatives, polyvinylanthracene, polyacenaphthylene, anthracene, pyrazoline, oxazole, triazole and hydrazone.

3. The photoconductive composition according to claim **2** wherein said charge-transfer molecular complex is selected from the group consisting of poly-N-vinylcarbzaole-tetrachloro-p-benzoquinone and poly-N-vinylcarbazole-tetracyanoquinodimethane.

4. The photoconductive composition according to claim **2** wherein said poly-N-vinylcarbazole derivative is nitrated poly-N-vinylcarbazole.

5. The photoconductive composition according to claim **1** wherein said chlorinated paraffin is in liquid state.

* * * * *