

[54] **PHOTOCONDUCTIVE LAYER WITH OVERCOAT OF DYE SENSITIZER**

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

[58] Field of Search **96/1.6, 1.5; 252/501**

[56] **References Cited**

UNITED STATES PATENTS

3,037,861	1/1962	Hoegl et al.	96/1.5
3,591,374	7/1971	Sens.	252/501 X
3,620,720	11/1971	Yamaguchi et al.	96/1.6 X

3,634,079	1/1972	Champ et al.	96/1.6 X
3,684,548	8/1972	Contois.	96/1.5

FOREIGN PATENTS OR APPLICATIONS

4,326,710	11/1968	Japan.	96/1.6
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[57] **ABSTRACT**

An electrophotographic element comprising a conductive support, an organic insulating layer attached to said conductive support, and a sensitizing organic layer contiguous to said organic insulating layer, said organic insulating layer having no sensitizers included therein and comprising a poly-N-alkenylcarbazole such as poly-N-vinylcarbazole or a nuclear substituted poly-N-vinylcarbazole, said sensitizing organic layer comprising an organic dye sensitizer. The electrophotographic element has high sensitivity to visible light.

24 Claims, 2 Drawing Figures

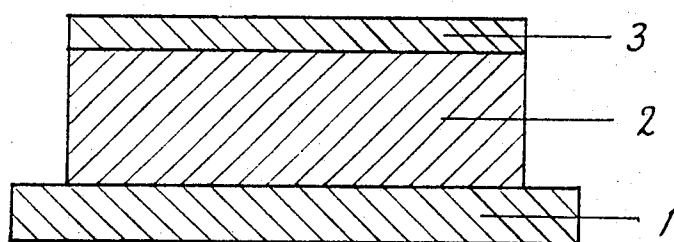


Fig. 1

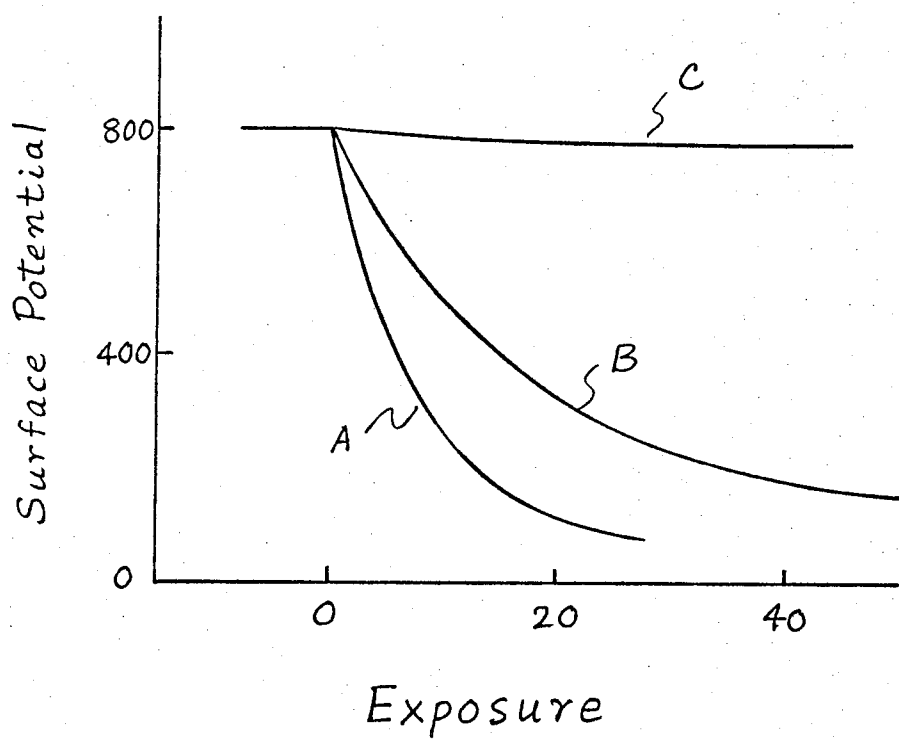


Fig. 2

PHOTOCONDUCTIVE LAYER WITH OVERCOAT OF DYE SENSITIZER

This invention relates to an electrophotographic element comprising organic materials, and more particularly to a novel electrophotographic element having a high sensitivity to visible light.

In electrophotography, an electrostatic latent image is formed by exposing a uniformly charged photoconductive layer to a light through or reflected from an original document. Said electrostatic latent image is developed by using a toner directly on the photoconductive layer or after being transferred to a dielectric layer, or is changed to a frost image by heating.

Selenium and zinc oxide are well known as inorganic photoconductive materials useful for electrophotography. Recently, much attention has been paid to organic photoconductive materials because of their excellent characteristics such as transparency, light weight, flexibility, and flat surface. However, the electrophotographic sensitivity of organic photoconductive materials is usually much lower than that of evaporated selenium photoconductive layer. The organic electrophotographic element having sensitizers distributed uniformly therein generally has a considerable residue potential in photo-decay process.

It is an object of this invention to provide an electrophotographic element having a high sensitivity to a visible light.

It is another object of this invention to provide a highly sensitive electrophotographic element which is transparent and flexible.

It is still another object of this invention to provide an electrophotographic element which shows little residue potential in the photo-decay process.

Details of this invention becomes apparent upon consideration of the following description taken together with the accompanying drawings in which:

FIG. 1 shows a section through an electrophotographic element according to this invention.

FIG. 2 shows sensitivity curves for a conventional electrophotographic element and a novel electrophotographic element of this invention.

It has been discovered according to this invention that an electrophotographic element comprising a conductive support, an organic insulating layer on said conductive support, and a sensitizing organic layer contiguous to said organic insulating layer, said sensitizing organic layer comprising an organic sensitizer, shows a high sensitivity to a visible light.

Referring to FIG. 1, a conductive support 1 supports an organic insulating layer 2 and a sensitizing organic layer 3.

The conductive support 1 may comprise any suitable conductive support. For example, a flexible film having a cuprous iodide layer or an evaporated conductive metal layer thereon can be used when flexibility and/or transparency is required. And further, a tin oxide-coated conducting glass or metal plate can be used when flexibility and/or transparency is not required.

The organic insulating layer 2 comprises at least one polymer selected from the group consisting of poly-N-vinylcarbazole, poly-N-alkenylcarbazole, and nucleus-substituted poly-N-vinylcarbazole, in accordance with the present invention. Addition of a plasticizer and polycarbonate into the organic insulating layer 2 is effective to improve mechanical properties of the layer

2. The plasticizer comprises chlorinated diphenyl, epoxy resin, chlorinated fatty acid ester, phthalic acid ester, or mixtures thereof. The amount of the plasticizer is less than 80 weight parts, preferably 20 to 40 weight parts relative to 100 weight parts of the polymer. Polycarbonate has the effect of improving the mechanical properties of the poly-N-vinylcarbazole, or nucleus-substituted poly-N-vinylcarbazole layer without reducing the transparency. The amount of polycarbonate to be added is less than 60 weight parts, preferably 10 to 40 weight parts relative to 100 weight parts of the polymer.

The organic insulating layer 2 has a thickness of 3 to 30 microns, preferably 5 to 20 microns and is obtained by the following method. A solution including aforesaid polymer in any solvent such as toluene, chlorobenzene, or dioxane is applied to any suitable conductive support by any suitable and available method such as knife, blade, or reverse-roll coating method and is dried at a temperature of 40° to 100°C, preferably 60° to 80°C for a time of more than 5 minutes to form an organic insulating layer in desired thickness. If necessary, the solution may further include a plasticizer and polycarbonate to improve mechanical properties of the organic insulating layer.

The sensitizing organic layer 3 comprises an organic sensitizer to generate photo-carriers upon illumination of visible light. A single use of said organic sensitizer is operable but the mechanical properties and the photosensitivity of resultant electrophotographic element is improved by incorporating said organic sensitizer with an organic matrix having an electrical resistivity higher than 10^{12} ohm-cm. A preferably organic matrix is polystyrene or polycarbonate. A thickness of said sensitizing organic layer 3 has an effect on the sensitivity of the resultant electrophotographic element and is in a thickness of 0.1 to 1 micron, preferably 0.3 to 0.6 micron. The sensitizing organic layer 3 comprises 0.1 to 10 weight parts, preferably 0.4 to 2 weight parts of an organic sensitizer relative to 100 weight parts of the polymer in said organic insulating layer 2.

The organic sensitizer comprises pyrylium salts described in U.S. Pat. No. 3,250,615, thiapyrylium salts described in U.S. Pat. No. 3,250,615, carbonium salts described in U.S. Pat. No. 3,575,698, benzopyrylium salts described in U.S. Pat. No. 3,526,502, benzopyrylium salt derivatives described in U.S. patent application Ser. No. 4,200 filed Jan. 20, 1970, or mixtures thereof.

Among the many sensitizers described above, the more preferable are a reaction product of 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate and 2-(p-methoxystyryl)-3-phenyl-4-methoxypyrene, 2-[(2'- α -phenyl-p-methoxystyryl)-4'-benzopyranylidene]methyl]-3-phenylbenzopyrylium perchlorate, and 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate. They produce a sensitizing organic layer 3 having spectral response more matched with a tungsten lamp and a high sensitivity. The reaction product of 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate and 2-(p-methoxystyryl)-3-phenyl-4-methoxypyrene is obtained from the reaction of these in hot 1,2-dichloroethane solution described in U.S. Pat. No. Application 4,200 filed Jan. 20, 1970, and the chemical structure of the reaction product has not been identified.

The organic insulating layer 2 is overcoated with a sensitizing organic layer 3. A solution including the aforesaid sensitizer, if necessary, aforesaid organic matrix having a high electrical resistivity in a solvent inert to the organic insulating layer is applied to the organic insulating layer by any suitable method such as whirler, blade, or kiss coating method and is dried to form a sensitizing organic layer. When the solution includes the organic matrix, the solution is dried at a temperature of 40° to 100°C, preferably 60° to 80°C for a time of more than 5 minutes. The solution including further polystyrene or polycarbonate is cured at a temperature of 80° to 160°C for a time of more than 5 minutes. Suitable solvent is alcohol such as methanol or ethanol, or ketone such as acetone or methyl-ethyl ketone, or butyl-acetate. Further, a sensitizing layer can be formed on the organic insulating layer by vacuum evaporation of aforesaid sensitizer.

In a conventional organic electrophotographic element, an organic photoconductive layer supported on a conductive support has organic sensitizers distributed uniformly therein. Even when the same polymer for example, poly-N-vinylcarbazole and the same organic sensitizer, for example, the benzopyrylium salt derivative, are used, the novel electro-photographic element has a higher sensitivity to visible light than that of the conventional organic electrophotographic element. The reason for the difference in the sensitivity between the novel electrophotographic element according to the present invention and the conventional electrophotographic element is not certain. A possible explanation is as follows: In the conventional electrophotographic element, the sensitizer distributed uniformly in the organic photoconductive layer acts as a trap to catch photo-carriers. On the other hand, the sensitizer in contact with the surface of the organic insulating layer as shown in FIG. 1 has no bad effect on the movement of photo-carriers in the organic insulating layer beneath the sensitizing layer. In the element of this invention, photo-carriers generated in the vicinity of the sensitizing layer may drift to the conductive support without being trapped. Thus, when the element of this invention is charged to a positive potential and then is exposed to visible light, the surface potential of the element dissipates rapidly and shows little residual potential. A conventional electro-photographic process for forming an electrostatic latent image on the element of this invention comprises a process of charging the element of this invention to a positive potential and exposing it to a light image. Said latent image is developed by using a toner directly on the surface of said element or after being transferred to a suitable dielectric layer, or is changed to a frost image by heating.

Photosensitivity of the element is defined as a half-decay exposure, said exposure is the exposure to reduce a surface potential of the element to a half of the surface potential in the dark. And further, the exposure to reduce a surface potential of the element to 20 percent of the surface potential in the dark is defined as 20 percent-decay exposure which also represents the photosensitivity. The smaller the half-decay or 20 percent-decay exposure, the more photosensitive the element.

Various embodiments of this invention will be shown in the following examples and should not be construed as limitative.

EXAMPLE 1

An electrophotographic element is first prepared. 1.0 gram of poly-N-vinylcarbazole (Luvican M-170, available from BASF Company) and 0.5 gram of chlorinated diphenyl (Kanechlor No. 400, available from Kanegafuchi Chemical Industrial Company) are dissolved in 10 milliliters of toluene to form a solution. The solution is applied to an aluminum plate by blade coating and is dried at 60°C for 5 minutes to obtain an organic insulating layer of about 10 microns in thickness. A methyl-ethyl ketone solution containing 1.0 gram of polystyrene (Dialex HF-55, available from Mitsubishi Chemical Company), 0.5 gram of chlorinated diphenyl and 0.1 gram of the reaction product of 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate and 2-(p-methoxystyryl)-3-phenyl-4-methoxypyrene is applied to the organic insulating layer and is heated at 100°C for 30 minutes to form a sensitizing organic layer of about 0.5 micron in thickness. The thus obtained electrophotographic element is then charged to a positive or a negative potential of about 800 volts by corona discharge means and exposed to a tungsten lamp (2,800°K.) The decay curve of the surface potential of the element is measured by an electrometer and is shown in FIG. 2. As shown in FIG. 2, the element of this invention has a photoresponse when charged to a positive potential (curve A) but has no photoresponse when charged to a negative potential (curve C). Half-decay exposure of the element is 6 lux seconds.

For comparison, a conventional electrophotographic element is prepared. A solution containing 1.0 gram of poly-N-vinylcarbazole, 0.5 gram of chlorinated diphenyl, and 5 milligrams of the sensitizer the same as above in 10 milliliters of toluene is applied to an aluminum plate by blade coating and dried at 60°C for 5 minutes to obtain a photo-conductive layer of about 10 microns in thickness. The amount of the sensitizer contained in said photoconductive layer is the same as that in the sensitizing organic layer of the above novel electrophotographic element. The thus obtained conventional electrophotographic element having the sensitizer distributed uniformly throughout the photoconductive layer is then charged to a positive or a negative potential of about 800 volts by corona discharge means and is exposed to a tungsten lamp. The measured decay curve of the surface potential is shown in FIG. 2. This conventional element has a photo-response when charged to a positive and a negative potential (curve B). The half-decay exposure of the element is 15 lux seconds. Thus, it is evident that the element of this invention is much more photosensitive than the conventional element.

In FIG. 2, surface potential of the element is indicated on the vertical axis in volt unit, while exposure is indicated along the horizontal axis in lux second unit.

EXAMPLE 2

Electrophotographic elements are prepared as in Example 1 except that here the sensitizer used is

1. 2,4-diphenyl-6-(α -amyl-3',4'-dimethoxystyryl)-pyrylium fluoborate.
2. tris-p-methoxyphenylcarbonium perchlorate, or
3. 2-[(2'- α -phenyl-p-methoxystyryl-4'-benzopyran-yl)-

dene)methyl]-3-phenylbenzopyrylium perchlorate.

and heating of the sensitizing organic layer of the element is performed at 100°C for 60 minutes. Half-decay exposure of these elements is shown in Table I.

For comparison, conventional elements having sensitizers distributed uniformly throughout the photoconductive layer are prepared as in Example 1 except that here the sensitizers used is the same as above and half-decay exposure of these is also shown in Table I.

Table I

Half-decay exposure (in lux seconds)		
Sensitizer	Conventional electrophotographic element	Novel electrophotographic element of this invention
(1)	30	14
(2)	50	18
(3)	15	6

EXAMPLE 3

Elements are prepared as in Example 1 except that here, the amount of the sensitizer in the sensitizing layer is varied from 1 to 100 weight parts relative to 100 weight parts of polystyrene (PS). Half-decay exposure of these elements is shown in Table II.

Table II

The amount of a sensitizer in the sensitizing layer versus half-decay exposure	
The amount of a sensitizer in the sensitizing layer (in weight parts relative to 100 weight parts of PS)	Half-decay exposure (in lux seconds)
1	32
2.5	14
3.5	11
5	8.2
10	6.0
15	6.5
20	7.8
30	10
50	18
100	30

EXAMPLE 4

Electrophotographic elements are prepared as in Example 1 except that here heating of the sensitizing layer is performed at a temperature of 60° to 160°C for 30 minutes or at 120°C for a time of 5 to 60 minutes.

Heating effect is shown in Tables III and IV in relation to half-decay exposure of these elements. It is evident that the sensitivity of the element of this invention is enhanced by heating. The sensitivity of the conventional element, however, can not be enhanced by heating.

Table III

Heating effect of the sensitizing layer at a temperature of 60 to 160°C for 30 minutes	
Heating temperature (in °C)	Half-decay exposure (in lux seconds)
20	32
60	8.4

Table III-Continued

Heating effect of the sensitizing layer at a temperature of 60 to 160°C for 30 minutes	
Heating temperature (in °C)	Half-decay exposure (in lux seconds)
70	7.4
80	6.9
90	6.2
100	6.0
110	6.0
120	6.2
130	6.2
140	6.4
150	6.9
160	7.8

Table IV

Heating effect of the sensitizing layer at 120°C for a time of 5 to 60 minutes	
Time of heating (in minutes)	Half-decay exposure (in lux seconds)
0	32
5	8.4
10	7.1
15	6.6
20	6.4
30	6.2
45	6.6
60	8.4

EXAMPLE 5

An element is prepared as follows. 1.0 gram of brominated poly-N-vinylcarbazole (monobromosubstituted compound described in U.S. Pat. No. 3,421,891), 0.3 gram of polycarbonate resin (Panlite L, available from Teijin Company), and 0.3 gram of epoxy resin (Epicote 828, available from Shell Oil Company) are dissolved in mixed solvent of 9 milliliters of chlorobenzene and 3 milliliters of 1,2-dichloroethane to form a solution. The solution is applied to a transparent conductive polyester film having cuprous iodide thereon by blade coating and is dried at 80°C for 20 minutes to obtain an organic insulating layer of about 8 microns in thickness. A sensitizing organic layer containing sensitizers of about 0.6 micron in thickness is formed on the organic insulating layer by applying a methyl-ethyl ketone solution containing 1.0 gram of polystyrene and 0.1 gram of the sensitizer the same as in Example 1 and by heating at 100°C for 10 minutes. This element is transparent and flexible. Half-decay exposure of the element is 5 lux seconds and 20 percent-decay exposure is 12 lux seconds. Little residue potential is observed in the decay process.

EXAMPLE 6

An element is prepared. An organic insulating layer of about 10 microns in thickness is formed on an aluminum plate as in Example 1 and is then exposed to ultra violet light. By this exposure, the layer becomes insoluble in a solvent such as toluene, chlorobenzene, or dioxane.

A sensitizing organic layer of about 0.5 micron in thickness is formed on the organic insulating layer by applying a 1,2-dichloroethane solution containing 1.0 gram of polycarbonate and 0.1 gram of 2-(p-

dimethylaminostyryl)-3-phenylbenzopyrylium perchlorate.

Half-decay exposure of this element is 8 lux seconds and 20 percent-decay exposure is 19 lux seconds.

EXAMPLE 7

An element is prepared as follows. An organic insulating layer of about 10 microns in thickness is formed on an aluminum plate as in Example 1. A sensitizing layer of about 0.1 micron in thickness is formed on the layer by the evaporation of tris-p-methoxyphenylcarbonium perchlorate.

The thus obtained element is then charged to a positive potential of about 1,200 volts by corona discharge and then exposed to a visible light. The surface potential of the element is observed to decay to nearly zero volts.

What is claimed is:

1. An electrophotographic element comprising in the following order a conductive support, an organic insulating layer on said conductive support and a sensitizing organic layer on said organic insulating layer, said organic insulating layer having no sensitizers included therein and comprising a poly-N-alkenylcarbazole, said sensitizing organic layer consisting essentially of an organic dye sensitizer.

2. An electrophotographic element according to claim 1, wherein said sensitizing organic layer consists essentially of an organic sensitizer selected from the group consisting of pyrylium salts, thiapyrylium salts, carbonium salts, benzopyrylium salts, benzopyrylium salt derivatives, and mixtures thereof.

3. An electrophotographic element according to claim 1, wherein said poly-N-alkenylcarbazole is brominated poly-N-vinylcarbazole.

4. An electrophotographic element according to claim 1, wherein said poly-N-alkenylcarbazole is poly-N-vinylcarbazole.

5. An electrophotographic element according to claim 3, wherein said sensitizing organic layer consists essentially of an organic sensitizer selected from the group consisting of pyrylium salts, thiapyrylium salts, carbonium salts, benzopyrylium salts, benzopyrylium salt derivatives, and mixtures thereof.

6. An electrophotographic element according to claim 5, wherein said organic sensitizer is in an amount of 0.1 to 10 weight parts relative to 100 weight parts of said polymer.

7. An electrophotographic element according to claim 6, wherein said organic insulating layer has a thickness of 3 to 30 microns.

8. An electrophotographic element according to claim 7, wherein said sensitizing organic layer is in a thickness of 0.1 to 1 micron.

9. An electrophotographic element according to claim 8, wherein said sensitizing organic layer is formed by overcoating of a solution comprising said organic sensitizer combined with an organic matrix having a high electrical resistivity and a solvent onto said organic insulating layer, said solvent comprising a member selected from the group consisting of methanol, ethanol, acetone, methyl-ethylketone and butylacetate.

10. An electrophotographic element according to claim 9, wherein said organic matrix is polystyrene.

11. An electrophotographic element according to claim 9 wherein said organic matrix is polycarbonate.

12. An electrophotographic element according to claim 9, wherein said organic sensitizer is the reaction product of 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate and 2-(p-methoxystyryl)-3-phenyl-4-methoxypyrene.

13. An electrophotographic element according to claim 9, wherein said organic sensitizer is 2-[(2'- α -phenyl-p-methoxystyryl)-4'-benzopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate.

14. An electrophotographic element according to claim 9, wherein said organic sensitizer is 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate.

15. An electrophotographic element according to claim 4, wherein said sensitizing organic layer consists essentially of an organic sensitizer selected from the group consisting of pyrylium salts, thiapyrylium salts, carbonium salts, benzopyrylium salts, benzopyrylium salt derivatives, and mixtures thereof.

16. An electrophotographic element according to claim 15, wherein said organic sensitizer is in an amount of 0.1 to 10 weight parts relative to 100 weight parts of said polymer.

17. An electrophotographic element according to claim 16, wherein said organic insulating layer has a thickness of 3 to 30 microns.

18. An electrophotographic element according to claim 17, wherein said sensitizing organic layer is in a thickness of 0.1 to 1 micron.

19. An electrophotographic element according to claim 18, wherein said sensitizing organic layer is formed by overcoating of a solution comprising said organic sensitizer combined with an organic matrix having a high electrical resistivity and a solvent onto said organic insulating layer, said solvent comprising a member selected from the group consisting of methanol, ethanol, acetone, methyl-ethylketone and butylacetate.

20. An electrophotographic element according to claim 19, wherein said organic matrix is polystyrene.

21. An electrophotographic element according to claim 19, wherein said organic matrix is polycarbonate.

22. An electrophotographic element according to claim 19, wherein said organic sensitizer is the reaction product of 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate and 2-(p-methoxystyryl)-3-phenyl-4-methoxypyrene.

23. An electrophotographic element according to claim 19, wherein said organic sensitizer is 2-[(2'- α -phenyl-p-methoxystyryl)-4'-benzopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate.

24. An electrophotographic element according to claim 19, wherein said organic sensitizer is 2-(p-methoxystyryl)-3-phenylbenzopyrylium perchlorate.

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