

Sept. 1, 1970

YOSHINOBU MURAKAMI ET AL

3,526,502

ELECTROPHOTOGRAPHIC MATERIAL

Filed May 4, 1967

2 Sheets-Sheet 1

FIG. 1

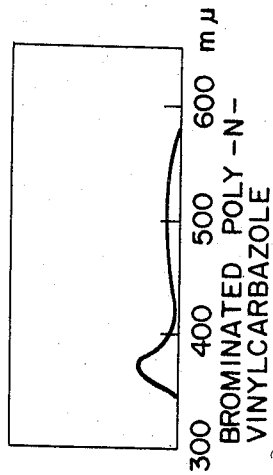


FIG. 3

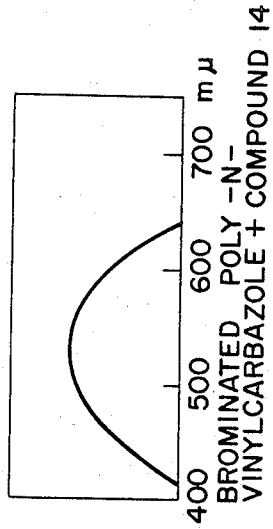


FIG. 2

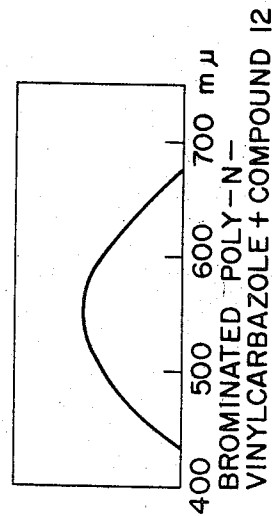
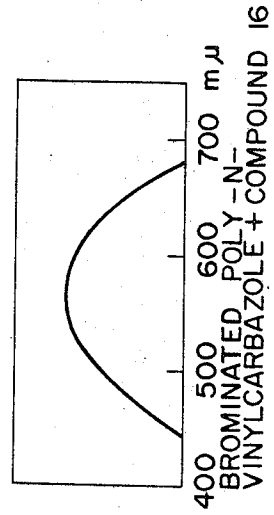


FIG. 4



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2 Sheets-Sheet 2

FIG. 7

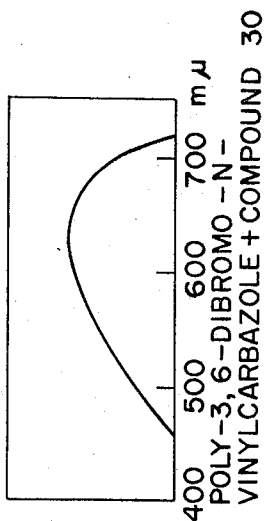


FIG. 8

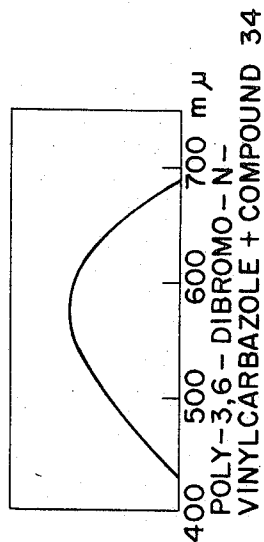


FIG. 5

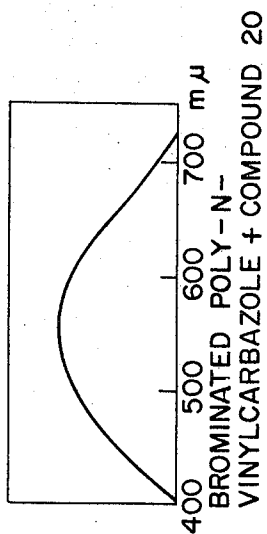
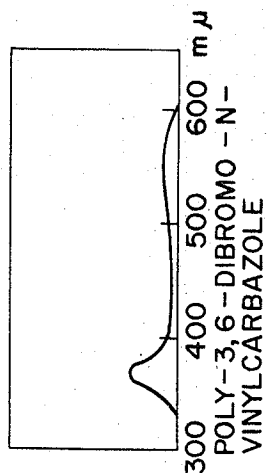


FIG. 6



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ELECTROPHOTOGRAPHIC MATERIAL

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U.S. Cl. 96—1.5

6 Claims

ABSTRACT OF THE DISCLOSURE

An improved electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a combination of a photoconductive polymeric compound and a benzopyrylium salt as a novel sensitizer, said photoconductive polymeric compound comprising at least one compound selected from the group consisting of poly-N-vinylcarbazole, poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene and polyvinylanthracene.

This invention relates to novel light-sensitive polymer layers and more particularly to electrophotographic light-sensitive polymer layers containing a benzopyrylium salt as a novel class of sensitizers of organic photoconductors.

Various light-sensitive layers are well known in the electrophotographic art for making copies of documents, drawings, transparencies, etc. These layers contain an organic photoconductive material, such as poly-N-vinylcarbazole, poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene, polyvinylanthracene, etc. These layers are non-conductors of electricity before exposure and become electrical conductors upon exposure.

It is necessary for the electrophotographic art that the photoconductive material has a high photoconductivity in the long wave length region of the visible spectrum. Such a photoconductive material makes it possible for the electrophotographic art to employ inexpensive and convenient light sources such as incandescent lamps in a reduced exposure time and to reproduce colored pictures. The photoconductive materials mentioned above, however, have usually a low photoconductivity and spectrum characteristics sensitive to a short wave length region of the exposure light and do not satisfy entirely the above requirement.

It is known that an addition of a so-called sensitizer can improve the above photoconductive materials in respect of photoconductivity and spectrum characteristics. Conventional sensitizers are dyestuff compounds, such as triarylmethane dyes, xanthene dyes, triazine dyes or acridine dyes, but the conventional sensitizers are not entirely satisfactory for improving the photoconductivity and the spectrum characteristics of the available photoconductive materials.

In addition to the high photoconductivity and spectrum characteristics sensitive to visible light, the electrophotographic art requires a high electric resistance of photoconductive materials in the dark. Conventional sensitizers are apt to increase the dark conductivity whereas they promote the photoconductivity. A high dark conductivity of photoconductive materials is not desirable because it results in a loss of the applied electrostatic charge in the dark.

An object of the invention is to provide electrophotographic materials having a high photoconductivity and spectrum characteristics sensitive to a long wave length region of the visible spectrum.

Another object of the invention is to provide electro-

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photographic materials having a high electric resistance in the dark.

These and other objects are accomplished by adding a benzopyrylium salt as a sensitizer to poly-N-vinylcarbazole, poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene or polyvinylanthracene, as a light-sensitive film-forming composition.

The invention is further explained in the following description with reference to the accompanying drawings wherein:

FIG. 1 represents the wedge spectrogram for an electrophotographic material coated with unsensitized 10 weight percent brominated poly-N-vinylcarbazole in chlorobenzene.

FIG. 2 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(α -isopropyl- ω -phenylbutadienyl) benzopyrylium perchlorate, said brominated poly-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 3 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate, said brominated poly-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 4 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(α -isopropyl- ω -phenylbutadienyl)-6-phenylbenzopyrylium perchlorate, said brominated poly-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

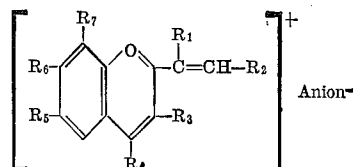
FIG. 5 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate, said brominated poly-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 6 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent poly-3,6-dibromo-N-vinylcarbazole in chlorobenzene.

FIG. 7 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of poly-3,6-dibromo-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate, said poly-3,6-dibromo-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane, and

FIG. 8 represents the wedge spectrogram for an electrophotographic material coated with 10 weight percent of poly-3,6-dibromo-N-vinylcarbazole sensitized with 0.02 weight percent of 2-(4'-methoxystyryl)-3-(4'-methoxyphenyl)benzopyrylium perchlorate, said poly-3,6-dibromo-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

The benzopyrylium salt compound (sensitizer) has the following formula:



wherein

R₁ is H, phenyl, or aliphatic group such as methyl, ethyl, propyl, isopropyl, butyl or tertiary butyl;

R₂ is aryl such as phenyl or 4-biphenyl, hydroxyphenyl such as 2-hydroxyphenyl, 4-hydroxyphenyl or 3,4-dihydroxyphenyl, alkoxyphenyl such as 4-methoxyphenyl or 3,4-dimethoxyphenyl, aminophenyl such as 4-dimethylaminophenyl or 4-diethylaminophenyl, styryl, substituted styryl such as 4-hydroxystyryl, 3,4-dihydroxystyryl, 4-methoxystyryl, 3,4-dimethoxystyryl or 4-dimethylaminostyryl, naphthyl or furyl;

R₃, R₅, R₆, R₇ each is H, aliphatic group such as methyl or ethyl, alkoxy group such as methoxy or ethoxy, hydroxy group, or aryl group such as phenyl or 4-methoxyphenyl;

R₄ is aryl group such as phenyl, 4-hydroxyphenyl or 4-methoxyphenyl, H, or aliphatic group such as styryl, alkoxyphenyl or hydroxystyryl;

anion is anionic function selected from the group consisting of fluoborate, chloride and perchlorate.

The preferred benzopyrylium salts are prepared generally by one of four methods. A first method (a modification of a method disclosed at J. Chem. Soc., 1935, p. 941) is based on the reaction of a phenol or phenol derivative with a β -dicarbonyl compound or α,β -unsaturated ketone in the presence of hydrogen chloride, sulfuric acid, ferric chloride or phosphorus pentachloride in solution of acetic or formic acid.

A second method comprises using an intermediate product prepared from a phenol and a coumarin derivative in the presence of phosphorus oxychloride or zinc chloride (a similar way to that disclosed at Helv. Chim. acta, 34, p. 1761 (1950)).

A third method (based on a method disclosed at J. Amer. Chem. Soc., 74, p. 3445 (1952)) is achieved by ring closure of an unsaturated ketone derivative prepared from an o-hydroxybenzaldehyde with a carbonyl compound in the presence of an alkali so as to form a benzopyrylium ring. The benzopyrylium ring is incorporated with an ethenyl radical by the reaction of active α -methylene radical in the 2-position of 2-alkylbenzopyrylium with an aromatic aldehyde.

A fourth method (based on a method disclosed at J. Chem. Soc., 1929, p. 936) is achieved in one step by both ring closure reaction and ethenylation reaction of an aromatic aldehyde with an unsaturated ketone derivative prepared from an o-hydroxybenzaldehyde with a carbonyl compound in the presence of an alkali.

Representative examples of the benzopyrylium salts according to the invention are listed in Table 1.

TABLE 1

Compound No.	Name of compound
1	2,4-dimethyl-7,8-dihydroxybenzopyrylium chloride.
2	2,4-bis (4'-methoxystyryl)-7,8-dihydroxybenzopyrylium chloride.
3	2,4-diphenyl-7,8-dihydroxybenzopyrylium chloride.
4	2-[α -isopropyl- β -(2'-hydroxynaphthyl(1')) ethenyl]-benzopyrylium chloride.
5	2-[α -isopropyl- β -(2'-hydroxynaphthyl(1')) ethenyl]-benzopyrylium perchlorate.
6	2-(2'-hydroxy-5'-phenylstyryl)-3-butyl-6-phenyl-benzopyrylium perchlorate.
7	2-(2'-hydroxystyryl)-3-butylbenzopyrylium perchlorate.
8	2-[β -(2'-hydroxynaphthyl(1')) ethenyl]-3-butyl-naphthopyrylium perchlorate.
9	2-(α -isopropyl-2'-hydroxystyryl)benzopyrylium perchlorate.
10	2-(α -isopropyl-2'-nitrostyryl)benzopyrylium perchlorate.
11	2-(α -isopropyl-4'-dimethylaminostyryl)benzopyrylium perchlorate.
12	2-(α -isopropyl- ω -phenylbutadienyl)benzopyrylium perchlorate.
13	2-[α -isopropyl- β -(2'-hydroxynaphthyl(1')) ethenyl]-6,7-dimethylbenzopyrylium perchlorate.
14	2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate.
15	2-[α -isopropyl- β -(2'-hydroxynaphthyl(1')) ethenyl]-6-phenylbenzopyrylium perchlorate.
16	2-(α -isopropyl- ω -phenylbutadienyl)-6-phenylbenzopyrylium perchlorate.
17	2-[α -isopropyl- ω -(3',4'-dimethoxyphenyl)butadienyl]-benzopyrylium perchlorate.

TABLE 1—Continued

Compound No.	Name of compound
18	2-[α -isopropyl- ω -furyl(2')butadienyl]benzopyrylium perchlorate.
19	2-(ω -phenylbutadienyl)-3-phenylbenzopyrylium perchlorate.
20	2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate.
21	2-(4'-dimethylaminostyryl)-3-phenylbenzopyrylium perchlorate.
22	2-[ω -furyl(2')butadienyl]-3-phenylbenzopyrylium perchlorate.
23	2-[ω -3',4'-dimethoxyphenyl]butadienyl]-3-phenylbenzopyrylium perchlorate.
24	2-(α -isopropyl-styryl)benzopyrylium perchlorate.
25	2-(α -isopropyl-4'-methoxystyryl)benzopyrylium perchlorate.
26	2-[α -isopropyl- β -(2'-hydroxynaphthyl(1')) ethenyl]-8-methoxybenzopyrylium perchlorate.
27	2-(α -isopropyl- ω -phenylbutadienyl)-8-methoxybenzopyrylium perchlorate.
28	2-(α -isopropyl-4'-methoxystyryl)-8-methoxybenzopyrylium perchlorate.
29	2-(ω -phenylbutadienyl)-3-phenyl-8-methoxybenzopyrylium perchlorate.
30	2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate.
31	2-[α -isopropyl- β -furyl(2')ethenyl]-8-methoxybenzopyrylium perchlorate.
32	2-[α -isopropyl- β -anthryl(9')ethenyl]benzopyrylium fluoborate.
33	2-(ω -phenylbutadienyl)-3-(4'-methoxyphenyl)benzopyrylium perchlorate.
34	2-(4'-methoxystyryl)-3-(4'-methoxyphenyl)benzopyrylium perchlorate.
35	2-(4'-dimethylaminostyryl)-3-phenylbenzopyrylium perchlorate.
36	2-(4'-methoxyphenyl)benzopyrylium perchlorate.

Table 2 lists additional information on the color and melting point of the novel compounds according to the invention.

TABLE 2

Compound No.	Color in dichloroethane	Melting point (°C.)
1	Orange	210
2	Reddish violet	190
3	do	187-189
4	do	212-213
5	Red	>250
6	Green	>250
7	Russet	>250
8	Brown	>250
9	Red	214-216
10	Brown	156-158
11	Deep blue	106-109
12	Russet	191-192
13	Reddish violet	>250
14	Red	219-220
15	Reddish violet	>250
16	do	215-217
17	Deep blue	>250
18	Violet	>250
19	Green	191-193
20	Reddish violet	227-229
21	Deep blue	221-222
22	Reddish violet	>250
23	Reddish green	210-212
24	Brown	98-100
25	Dark red	138-140
26	do	251-252
27	do	201-202
28	Brown	115-117
29	Blue	204-207
30	Reddish violet	144-146
31	Dark red	175-177
32	Brown	243-245
33	Reddish violet	173-175
34	do	183-185
35	Blue	>250
36	Yellow	195-196

A simple exchange reaction makes it possible for the anionic function of the benzopyrylium salt compounds to be Cl⁻, BF₄⁻ or ClO₄⁻.

Following description will explain a practical method for making benzopyrylium salts with reference to the exemplary compounds. The details of the preparation of other compounds will be apparent to those skilled in the art from the preceding disclosure and the following illustrative examples of preparation methods of various compounds according to the invention:

(a) 2,4-diphenyl-7,8-dihydroxybenzopyrylium chloride

To a solution of 25 grams of pyrogallol and 42 grams of benzalacetophenone in 500 milliliters of dry ethanol is added 49 grams of chloranil. The solution is then saturated with dry hydrogen chloride and allowed to stand overnight

at room temperature (about 20° to about 30° C.), and then it is poured into ether to form a precipitate. The precipitate is collected by filtration, washed thoroughly with ether and then dried at a reduced pressure ranging from 2 to 10 mm. Hg. Recrystallization from 40% methanol containing a small amount of hydrogen chloride yields 2 grams of russet crystals which melt at 187° to 190° C. (decomp.). The crystals give a reddish violet solution in dichloroethane.

(b) 2-(4'-methoxyphenyl)benzopyrylium perchlorate

A mixture of 14.6 grams of coumarin, 15 grams of dry ZnCl_2 and 50 milliliters of POCl_3 is heated at 80° C. in a water-bath for 35 minutes and is dissolved in 10.8 grams of anisole. The solution is again heated at 80° C. for 2 hours. After standing for several hours, the solution is incorporated with 150 milliliters of glacial acetic acid so as to form a precipitate. The precipitate is collected, washed with glacial acetic acid and then washed with ether. The crude product is dissolved in 50 milliliters of 10% perchloric acid. After several hours, a pure product is obtained as a precipitate of yellow crystals having a melting point of 195° to 196° C.

(c) 2-[α -isopropyl- β -(2'-hydroxynaphthyl(1'))-ethenyl]benzopyrylium perchlorate

To a cold solution of 10 grams of 2-hydroxystyryl isobutyl ketone and 8.5 grams of 2-naphthol-1-aldehyde is added 12 grams of 60% perchloric acid. The solution is ice-cooled and then is slowly saturated with dry hydrogen chloride which imparts a deep red color to the solution. The deep red solution is kept at 0° C. overnight, whereupon benzopyrylium salt precipitates. The precipitated benzopyrylium salt is then collected by filtration, washed thoroughly with ether and dried at a reduced pressure ranging from 2 to 10 mm. Hg. Recrystallization from nitrobenzene gives 5 grams of metallic lustrous needles which melts about 250° C. while darkening gradually. The needles give a red solution in dichloroethane.

(d) 2-(α -isopropyl- ω -phenylbutadienyl)-benzopyrylium perchlorate

To a cold solution of 4 grams of 2-hydroxystyryl isobutyl ketone and 2.7 grams of cinnamaldehyde in 15 milliliters of ether is added 6 grams of 60% perchloric acid. The solution is ice-cooled and then is slowly saturated with dry hydrogen chloride to obtain a deep red solution. The deep red solution is kept at 0° C. for one day so as to form a precipitate. The precipitate is then collected by filtration, washed with ether and dried at reduced pressure ranging from 2 to 10 mm. Hg. Recrystallization from a solvent of four weight parts of methanol and one weight part of dichloroethane gives 2.2 grams of red needles having a melting point of 191° to 192° C. The needles give a russet-colored solution in dichloroethane.

(e) 2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate

To a cold solution of 12 grams of 2-hydroxystyryl α -phenyl methyl ketone and 6.8 grams of anisaldehyde in a mixed solvent of 100 milliliters of ether and 100 milliliters of tetrahydrofuran is added 15 grams of 60% perchloric acid. Precipitation starts when the solution is saturated with dry hydrogen chloride. The solution and precipitate are then allowed to stand overnight in an ice-box, and then the resulting precipitate is collected by filtration, washed thoroughly with ether and dried at reduced pressure ranging from 2 to 10 mm. Hg. The obtained crude product is recrystallized twice from a solvent consisting of three weight parts of methanol and one weight part of dichloroethane to yield 3 grams of lustrous needles, having a melting point of 228° to 229° C. The needles give a reddish violet solution in dichloroethane.

It has been discovered according to the invention that the compounds listed in Table 1 are sensitizing agents

which can improve the photoconductivity and the spectrum characteristics of poly-N-vinylcarbazole, poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene and polyvinylanthracene. These polymers, except brominated poly-N-vinylcarbazole, are prepared in a per se well-known method. The brominated poly-N-vinylcarbazole can be prepared by the following method: To the solution of 20 grams of poly-N-vinylcarbazole in 450 milliliters of chlorobenzene, there is added 18.44 grams of N-bromosuccinimide and 0.173 gram of benzoyl peroxide. The mixture is heated at 80° C. for 2 hours while being stirred thoroughly, after which it is poured into methanol to obtain a white polymer. The white polymer is dissolved in chlorobenzene and again poured into methanol for purification. The pure polymer thus obtained as a precipitate exhibits upon elementary analysis a halogen content of 29.87 weight percent which approximates the value calculated, i.e. 29.44 weight percent of the monobromosubstituted product from poly-N-vinylcarbazole. This indicates that the polymer obtained is a monobromosubstituted product. The degree of bromination varies from 50 mole percent to 200 mole percent according to reaction conditions.

The novel sensitizer comprising at least one compound from the group listed in Table 1 is dissolved in a suitable solvent, such as methanol, ethanol, dichloroethane, methylene chloride, chloroform, or a combination thereof, and is added to the solution of the photoconductive polymer described above. The amount of the sensitizer added is from 0.01 to 2.0 weight parts to 100 weight parts of the photoconductive polymer. Preferable amount thereof is from 0.1 to 2.0 weight parts to 100 weight parts of the photoconductive polymer.

For the preparation of the photoconductive insulating layers, a said solution of the photoconductive polymer and the benzopyrylium salt in a suitable solvent is applied to the supports in the usual manner, for example, by spraying, by direct application, by means of blade coating, by means of whirler coating, etc., and then dried so as to produce a homogenous photoconductive insulating layer on the electroconductive support. Operable solvents are benzene, toluene, chlorobenzene, dioxane, methylene chlorides, dichloroethane and combinations thereof. Said solution may be incorporated with suitable plasticizers and/or organic colloids for improving the flexibility and strength of the photoconductive polymer. Operable plasticizers are as follows: chlorinated diphenyl, dimethyl phthalate, diethyl phthalate and octyl phthalate. Operable organic colloids are as follows: natural and synthetic resins, e.g. phenol resin, phenol resin modified with rosin, polyvinyl acetal, polyvinyl butyral, polyvinyl cinnamate, polycarbonate resin. Operable materials for electroconductive supports may be made of any materials which satisfy the requirement of the electrophotographic art, e.g. metal plate or glass plate having NESA coating, plate or foils made of electrically conductive resins or coated with evaporated thin metal layer. The transparent support can produce a transparent electrophotographic plate, foil or film. After an electrostatic charge has been applied, i.e., after the layer has been charged positively or negatively by means of a corona discharge, the layer becomes light sensitive.

The reproduction of images by electrophotographic methods is carried out as follows: when the photoconductive layer has been charged by means of a corona discharge apparatus, the support with the sensitized layer is exposed to light under a master and is then dusted over in a known manner with a resin powder colored with carbon black. The image that now becomes visible can easily be wiped off. It can also be fixed by heating at about 120° C. From positive masters, positive images characterized by good contrast are produced.

It has been further discovered according to the invention that the benzopyrylium salts polymerize N-vinylcarbazole or 3,6-dibromo-N-vinylcarbazole for obtaining

a high polymer. For example, to a solution of 1 gram of N-vinylcarbazole which is dissolved in 10 milliliters of dichloroethane is added 0.0003 gram of 2-(α -isopropyl- ω -phenylbutadienyl)benzopyrylium perchlorate which is dissolved in 0.1 milliliter of dichloroethane. After standing at 25° C. for 30 minutes, the solution is poured into methanol. The poly-N-vinylcarbazole obtained as a white precipitate has a molecular weight of a million and is prepared in a 98 weight percent yield.

3,6-dibromo-N-vinylcarbazole can be treated by the same procedure as mentioned above and is obtained as a white polymer in a high yield. The other benzopyrylium salts can be similarly used as an initiator of N-vinylcarbazole or 3,6-dibromo-N-vinylcarbazole polymerization.

Thus, the benzopyrylium salts discovered according to the invention can be used as a sensitizing agent and as an initiator of polymerization. Such two abilities make it possible to prepare an electrophotographic layer in the following manner: To a solution of 1 gram of 3,6-dibromo-N-vinylcarbazole dissolved in 10 milliliters of methylene chloride is added 0.001 gram of 2-(α -isopropyl- ω -phenylbutadienyl)-6-7-dimethylbenzopyrylium perchlorate which is dissolved in 0.1 milliliter of methylene chloride. After standing at 25° C. for an hour, the solution is directly applied to an aluminum plate by means of blade coating. Thus, an electrophotographic plate improved in the photosensitive properties can be easily obtained.

It has been discovered according to the invention that more preferable electrophotographic materials can be prepared by a combination of brominated poly-N-vinylcarbazole and, as benzopyrylium salt, at least one compound selected from the group consisting of

2-(α -isopropyl- ω -phenylbutadienyl)benzopyrylium perchlorate,
2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate,
2-(α -isopropyl- ω -phenylbutadienyl)-6-phenylbenzopyrylium perchlorate,
2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate,
2-[α -isopropyl- β -(2'-hydroxynaphthyl(1'))ethenyl]-8-methoxybenzopyrylium perchlorate,
2-(α -isopropyl- ω -phenylbutadienyl)-8-methoxybenzopyrylium perchlorate,
2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate and
2-(4'-methoxystyryl)-3-(4''-methoxyphenyl)benzopyrylium perchlorate.

Further, according to the invention, more preferable electrophotographic material can be prepared by a combination of poly-3,6-dibromo-N-vinylcarbazole and, as benzopyrylium salt, at least one compound selected from the group consisting of

2-(α -isopropyl- ω -phenylbutadienyl)benzopyrylium perchlorate,
2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate,
2-(α -isopropyl- ω -phenylbutadienyl)-6-phenylbenzopyrylium perchlorate,
2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate,
2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate and
2-(4'-methoxystyryl)-3-(4''-methoxyphenyl)benzopyrylium perchlorate.

The invention is still further illustrated with reference to the following illustrative examples.

EXAMPLE 1

1 gram of poly-N-vinylcarbazole and 0.004 gram of a benzopyrylium salt listed in Table 1 are dissolved in

10 milliliters of methylene chloride. The solution is applied to an aluminum plate by means of blade coating and is dried to form a layer of 10 μ in thickness. After the said aluminum plate provided with the layer is charged positively by means of corona discharge with a charging device maintained at approximately 6000 volts in the dark, it is placed under a positive master and is exposed to a 100 w. tungsten lamp at an illumination of 50 luxes, and the said plate is powdered over with a developer in a per se known manner. This developer consists of toner and carrier. The toner consists of a low melting-point polystyrene, colophony and carbon-black. The toner is mixed with a carrier substance having such nature that the toner becomes triboelectrically charged with a charge opposite to that produced on the plate. A positive image is produced and is fixed by slight heating. In Table 3 are shown the optimum amounts of exposure in lux-second units.

TABLE 3

Compound number:	Optimum exposure (lux.sec.)
None	20,000
14	70
16	55
30	32
34	42

EXAMPLE 2

1 gram of poly-3,6-dibromo-N-vinylcarbazole and 0.002 gram of a benzopyrylium salt listed in Table 1 are dissolved in 10 milliliters of dichloroethane. The solution is applied to an aluminum plate and is dried to form a layer of 10 μ in thickness. An electrophotographic image is produced in the same way as that described in Example 1. In Table 4 are shown the optimum amounts of exposure in lux-second units to produce exactly the original images.

TABLE 4

Compound number:	Optimum exposure (lux.sec.)
None	5000
12	27
14	35
16	35
20	22
30	25
34	22

It is clear from Table 4 and FIGS. 6 to 8 that the novel sensitizers improve the photoconductivity and the spectrum characteristics of poly-3,6-dibromo-N-vinylcarbazole.

EXAMPLE 3

1 gram of brominated poly-N-vinylcarbazole and 0.1 gram of chlorinated aliphatic acid ester (commercially available as "Adecasizer S-3"), 0.2 gram of epoxy resin (commercially available as "Epon 828"), 0.5 gram of polycarbonate resin (commercially available as "Panlite-C") and 0.003 gram of a benzopyrylium salt listed in Table 1 are dissolved in a mixed-solvent of 8 milliliters of chlorobenzene and 2 milliliters of dichloroethane. This solution is applied to an aluminum plate or to a cellulose diacetate film sheet having a vacuum-evaporated film of cuprous iodide, by means of a blade coating and dried to form a layer of 12 μ in thickness. On these supports, electrophotographic images are produced in the same way as that described in Example 1. Table 5 shows the optimum amounts of exposure in lux-second units to reproduce exactly the original images.

TABLE 5

Compound No.	Optimum exposure on aluminum plate (lux.sec.)	Optimum exposure on CuI film (lux.sec.)
None.....	80,000	90,000
4.....	70	75
5.....	35	65
6.....	36	53
9.....	360	480
10.....	685	632
12.....	85	42
13.....	75	165
14.....	47	47
15.....	43	110
16.....	35	40
19.....	260	145
20.....	25	27
23.....	505	225
24.....	175	185
25.....	62	62
26.....	40	60
27.....	45	52
28.....	210	210
29.....	255	275
30.....	35	42
31.....	110	90
33.....	125	117
34.....	37	45
35.....	500	500

It is clear from Table 5 and FIGS. 1 to 5 that the novel sensitizers improve the photoconductivity and the spectrum characteristics of brominated poly-N-vinylcarbazole.

EXAMPLE 4

1 gram of polyacenaphthylene and 0.6 gram of chlorinated diphenyl and 0.005 gram of a benzopyrylium salt listed in Table 1 are dissolved in 10 milliliters of dichloroethane. The solution is applied to an aluminum plate by means of whirler coating and is dried to form a layer of 4 μ in thickness. An electrophotographic image is produced in a similar way to that described in Example 1. Table 6 shows the optimum amounts of exposure in lux-second units to reproduce exactly the original images.

TABLE 6

Compound number:	Optimum exposure (lux.sec.)
None	200,000
12	140
14	300
16	140
20	80
30	450
34	360

EXAMPLE 5

1 gram of poly-9-vinylanthracene and 0.5 gram of chlorinated diphenyl and 0.005 gram of a benzopyrylium salt listed in Table 1 are dissolved in 10 milliliters of methylene chloride. The solution is applied to an aluminum plate by means of whirler coating and is dried to form a layer of 3 μ in thickness. An electrophotographic image is produced in a similar way to that described in Example 1. Table 7 shows the optimum amounts in lux-second units of exposure to reproduce exactly the original images.

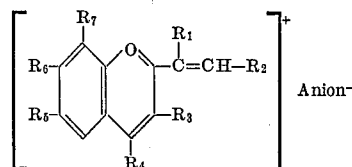
TABLE 7

Compound number:	Optimum exposure (lux.sec.)
None	47,000
12	240
14	280
16	140
20	95
30	550
34	875

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

Having thus disclosed the invention, what is claimed is:

1. An electrophotographic material comprising a conductive support layer and a photoconductive insulating layer, the latter comprising a combination of a photoconductive polymeric compound and a sensitizer having the following chemical formula



wherein

R₁ is H, phenyl or alkyl;

R₂ is phenyl, hydroxyphenyl, biphenyl, alkoxyphenyl, aminophenyl, styryl, substituted styryl, naphthyl or furyl;

R₃, R₅, R₆, R₇ each is H, styryl or substituted styryl, alkoxy, hydroxy, or aryl;

R₄ is aryl, H, or alkyl;

the anion is an anionic function selected from the group consisting of fluoborate, chloride and perchlorate; said photoconductive polymeric compound comprising at least one compound selected from the group consisting of poly-N-vinylcarbazole, poly-3,6-dibromo-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene and polyvinylanthracene.

2. An electrophotographic material as in claim 1 wherein

R₁ is selected from the group consisting of H, phenyl, methyl, ethyl, propyl, isopropyl, butyl or tertiary butyl;

R₂ is selected from the group consisting of phenyl, 4-biphenyl, 2-hydroxyphenyl, 4-hydroxyphenyl, 3,4-dihydroxyphenyl, 4-methoxyphenyl, 3,4-dimethoxyphenyl, 4-dimethylaminophenyl, 4-diethylaminophenyl, styryl, 4-hydroxystyryl, 3,4-dihydroxystyryl, 4-methoxystyryl, 3,4-dimethoxystyryl, 4-dimethylaminostyryl, naphthyl and furyl;

R₃, R₅, R₆, R₇ are selected from the group consisting of H, methyl, ethyl, methoxy, ethoxy, hydroxy, phenyl, 4-methoxyphenyl;

R₄ is selected from the group consisting of phenyl, 4-hydroxyphenyl, 4-methoxyphenyl, H, styryl, alkoxy-styryl, and hydroxystyryl;

the anion is selected from the group consisting of fluoborate, chloride and perchlorate.

3. An electrophotographic material according to claim 1, wherein said sensitizer comprises at least one compound selected from the group consisting of

2-(α -isopropyl- ω -phenylbutadienyl)benzopyrylium perchlorate,

2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate,

2-(α -isopropyl- ω -phenylbutadienyl)-6-phenylbenzopyrylium perchlorate,

2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate,

2-[α -isopropyl- β -(2'-hydroxynaphthyl(1'))ethenyl]-8-methoxybenzopyrylium perchlorate,

2-(α -isopropyl- ω -phenylbutadienyl)-8-methoxybenzopyrylium perchlorate,

2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate, and

2-(4'-methoxystyryl)-3-(4''-methoxyphenyl)benzopyrylium perchlorate.

4. An electrophotographic material according to claim 3, wherein said combination comprises 100 weight parts of photoconductive polymeric compound and 0.01 to 2.0 weight parts of sensitizer.

5. An electrophotographic material according to claim 3, wherein said combination is a combination of 100

weight parts of brominated poly-N-vinylcarbazole and 0.01 to 2.0 weight parts of said sensitizer.

6. An electrophotographic material according to claim 1, wherein said combination is a combination of 100 weight parts of poly-3,6-dibromo-N-vinylcarbazole and 0.01 to 2.0 weight parts of a sensitizer, said sensitizer comprising at least one compound selected from the group consisting of

- 2-(α -isopropyl- ω -phenylbutadienyl)-benzopyrylium perchlorate,
- 2-(α -isopropyl- ω -phenylbutadienyl)-6,7-dimethylbenzopyrylium perchlorate,
- 2-(α -isopropyl- ω -phenylbutadienyl)-6-phenyl-benzopyrylium perchlorate,
- 2-(4'-methoxystyryl)-3-phenylbenzopyrylium perchlorate,
- 2-(4'-methoxystyryl)-3-phenyl-8-methoxybenzopyrylium perchlorate, and

2-(4'-methoxystyryl)-3-(4''-methoxyphenyl)benzopyrylium perchlorate.

References Cited

UNITED STATES PATENTS

3,250,615 5/1966 Van Allan et al. ----- 96—1

FOREIGN PATENTS

229,679 3/1959 Australia.
964,875 7/1964 Great Britain.

OTHER REFERENCES

J. Chem. Soc., 1935, pp. 941-943.

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