

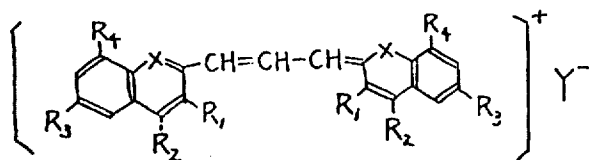
- [54] **ORGANIC PHOTOCONDUCTIVE LAYER SENSITIZED WITH TRIMETHINE COMPOUND**
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- [58] **Field of Search**..... 96/1.6, 1.5, 1.7; 252/501

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 Reynolds, G. A. et al., Def. Pub. of S.N. 235,845 filed 3-17-72, published in 904 O.G. 277 on 11-21-72, Def. Pub. No. T904,277.

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[57] **ABSTRACT**

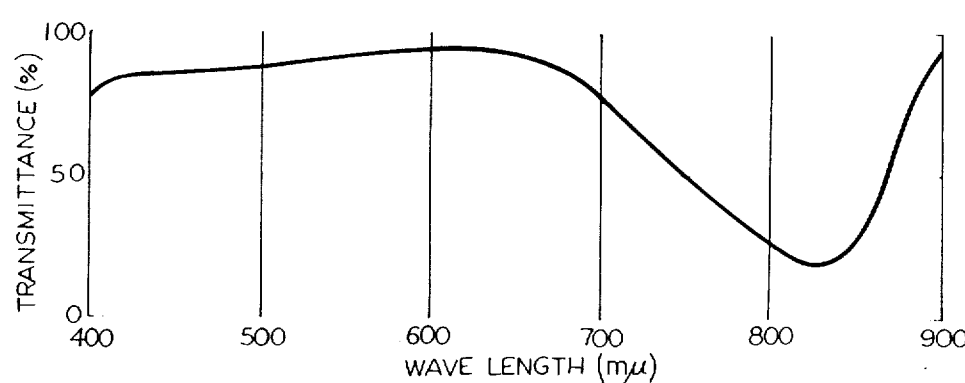
The present invention relates to organic photoconductive layers responsive to long wavelengths comprising a combination of an organic photoconductor and a sensitizer having the following chemical formula.

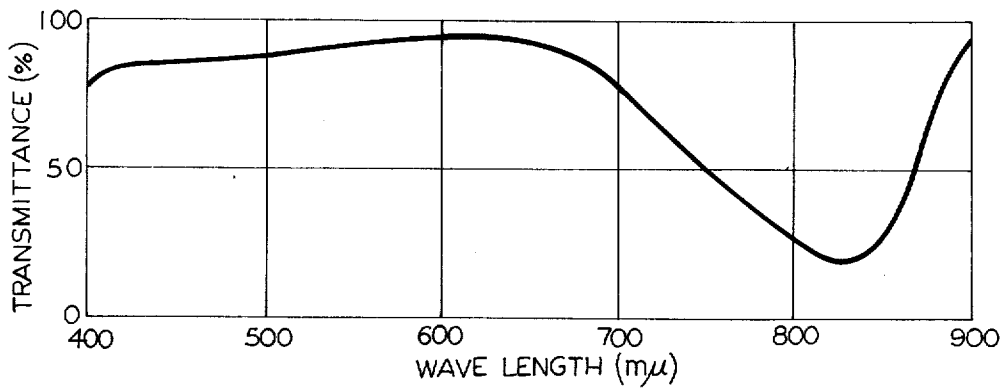


wherein  
 R is hydrogen or phenyl;  
 R is hydrogen, phenyl, 4-methoxyphenyl, naphthyl, 2-methoxynaphthyl (1) or 4-methoxynaphthyl (1);  
 R is hydrogen, methoxy, nitro or phenyl;  
 R is hydrogen or methoxy;  
 X is oxygen or sulfur atom;  
 and Y is perchlorate.

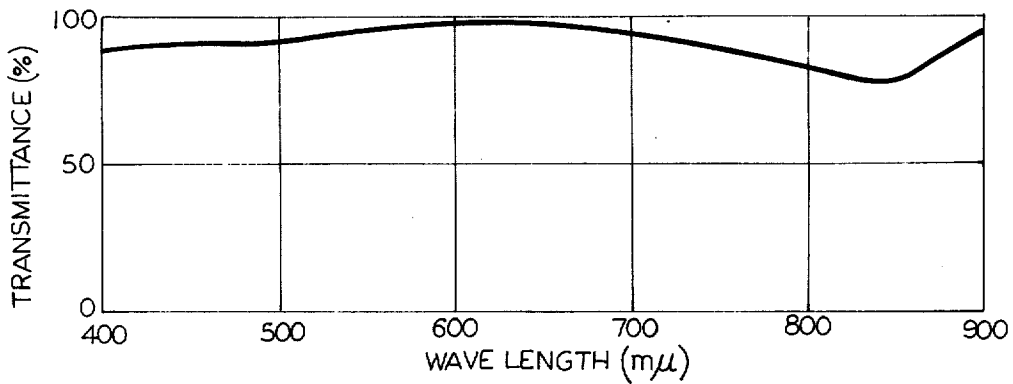
5 Claims, 9 Drawing Figures

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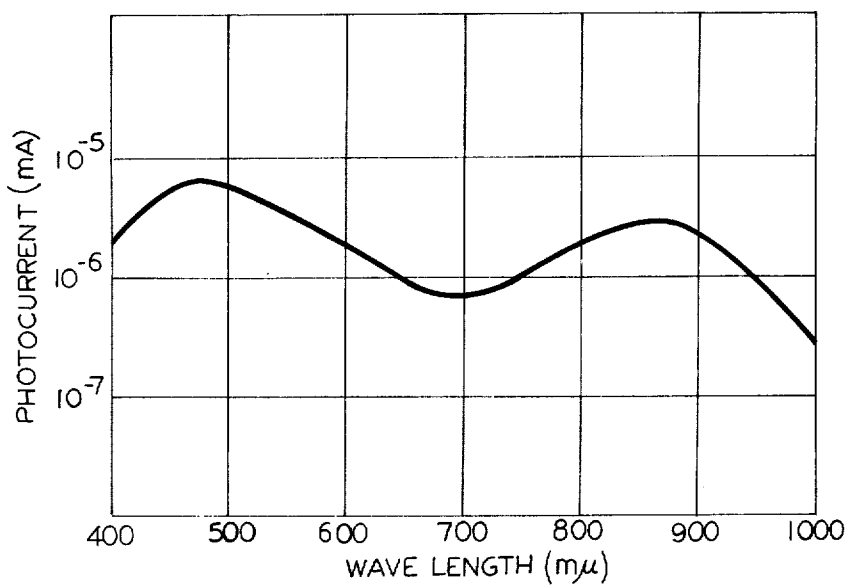




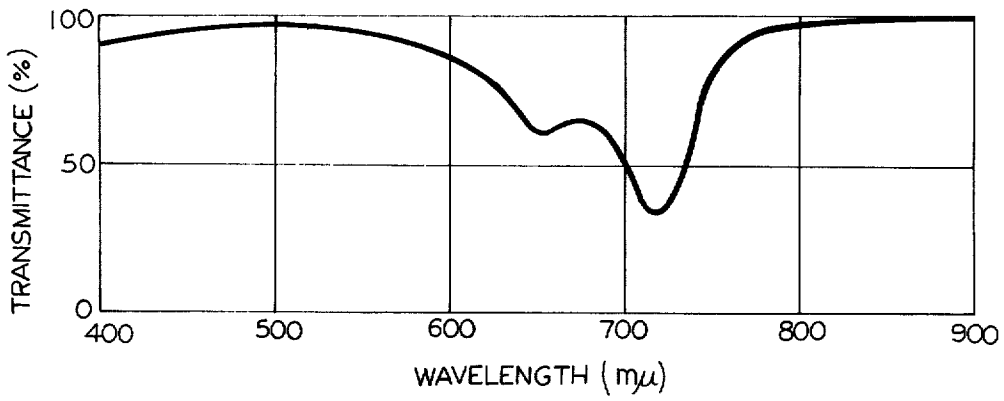
**FIG. 1**



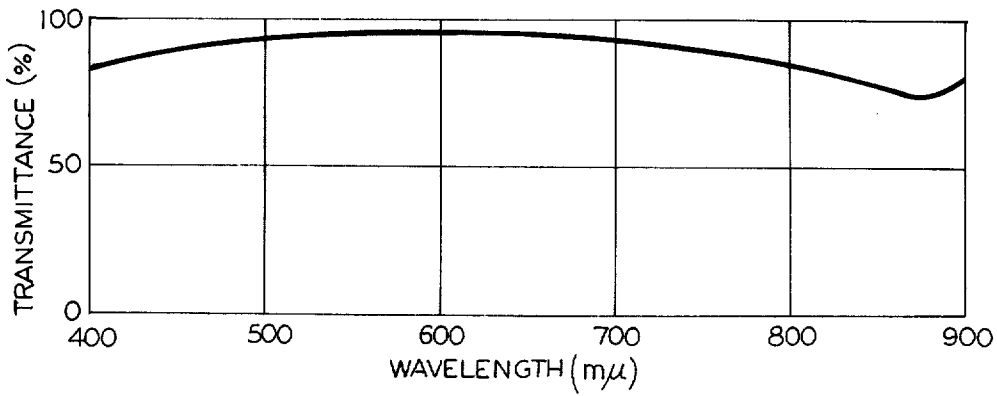
**FIG. 2**



**FIG. 9**

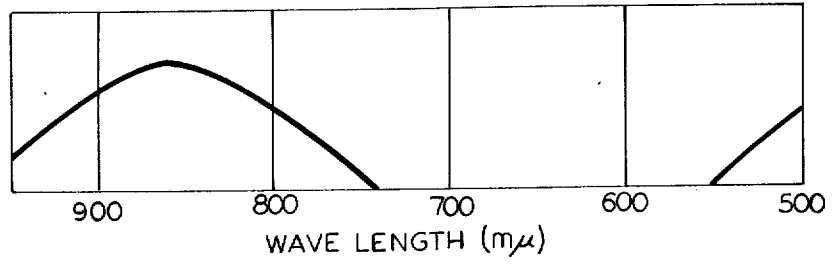


**FIG. 3**

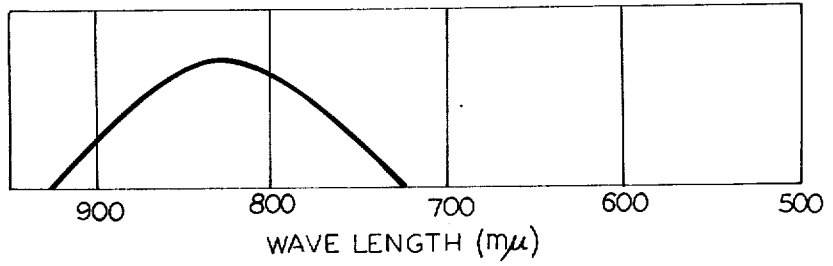


**FIG. 4**

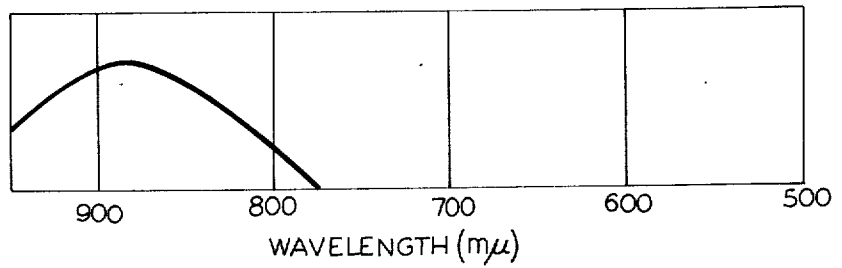
**FIG. 5**



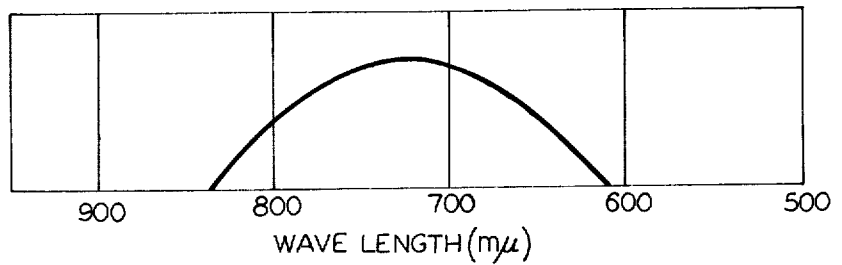
**FIG. 6**



**FIG. 7**



**FIG. 8**



## ORGANIC PHOTOCONDUCTIVE LAYER SENSITIZED WITH TRIMETHINE COMPOUND

This invention relates to photoconductive layers and more particularly to photoconductive polymer layers containing as a novel sensitizer, a trimethine compound.

Many kinds of organic photoconductive polymer layers are well known in the electrophotographic art for making copies of documents, drawings, transparencies, etc. It is necessary for the electrophotographic art that the photoconductive layer has a high photoconductivity in the long wavelength region of the visible spectrum or the near infra-red wavelength region. Such a photoconductive layer makes it possible for the electrophotographic art to employ an inexpensive and convenient light source such as a tungsten filament lamp in a reduced exposure time.

Interest in organic photoconductor cells has increased in the field of electronics, computers, high speed data recording and detecting systems. The applications mentioned above require a highly sensitive and transparent organic photoconductor preferably an organic photoconductive film-forming polymer.

The well-known organic photoconductive polymers are poly-N-vinylcarbazole, halogenated poly-N-vinylcarbazole, polyacenaphthylene, polyvinylanthracene, etc. The layers containing these photoconductive polymers are non-conductors of electricity before exposure and become electrical conductors upon exposure. It is known that an addition of a so-called sensitizer can improve photoconductivity and spectrum characteristics of the above photoconductive polymer. Conventional sensitizers are dyestuff compounds, such as 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 photoconductive polymer.

An object of the invention is to provide an organic photoconductive layer having a high photoconductivity.

Another object of the invention is to provide an organic photoconductive layer having sensitivity to the long wavelength region of the visible spectrum or to the near-infrared wavelength region.

Another object of the invention is to provide a preparation method of particularly effective new class sensitizers of organic photoconductor, said sensitizers having a trimethine structure containing a certain substituted benzopyrylium or benzothiapyrylium salt.

Another object of the invention is to provide a transparent photoconductive layer.

Still other objects will be apparent from the following specification and claims.

These and other objects are accomplished by the use of photoconductive film-forming compositions comprising a photoconductive polymer and a novel trimethine compound.

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

FIG. 1 represents the absorption spectrum of 2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzothiapyrylidene) propenyl]-3-phenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate in dichloroethane solution.

FIG. 2 represents the absorption spectrum of poly-N-vinylcarbazole film (10 microns in thickness) contain-

ing 0.2 mole percent of 2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzothiapyrylidene) propenyl]-3-phenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate.

FIG. 3 represents the absorption spectrum of poly-N-vinylcarbazole film (10 microns in thickness) containing 0.2 mole percent of 2-[3'-(3''-phenyl-2''-benzopyrylidene) propenyl]-3-phenylbenzopyrylium perchlorate.

FIG. 4 represents the absorption spectrum of poly-N-vinylcarbazole film (10 microns in thickness) containing 0.2 mole percent of 2-[3'-3'',6''-diphenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzothiapyrylidene propenyl]-3,6-diphenyl-4-(4'-methoxynaphthyl(1'))benzothiapyrylium perchlorate.

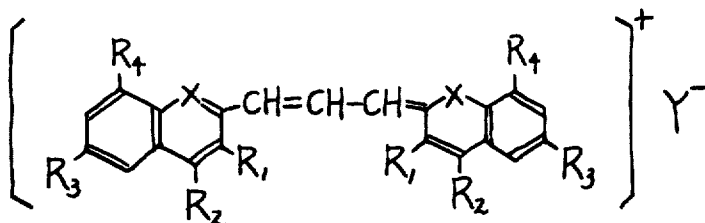
FIG. 5 represents the wedge spectrogram for an electrophotographic material coated with a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-[3'-(3'-phenyl-4''-p-methoxyphenyl-2''-benzothiapyrylidene) propenyl]-3-phenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a mixed 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 a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-[3'-(3'',6''-diphenyl-2''-benzopyrylidene) propenyl]-3,6-diphenylbenzopyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a mixed solvent of four weight parts of chlorobenzene and one weight part of dichloroethane. FIG. 7 represents the wedge spectrogram for an electrophotographic material coated with a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-[3'-3'',6''-diphenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzothiapyrylidene propenyl]-3,6-diphenyl-4-(4'-methoxynaphthyl(1'))benzothiapyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a mixed solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 8 represents the wedge spectrogram for an electrophotographic material coated with a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-[3'-(3''-phenyl-2''-benzopyrylidene) propenyl]-3-phenylbenzopyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a mixed solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 9 represents the spectral response of the photocurrent of the photoconductor cell (sandwich type cell) which is fabricated in the following: a transparent NESA conducting glass, a photoconductive polymer layer consisting of 0.2 mole percent of 2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzothiapyrylidene) propenyl]-3-phenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate in poly-N-vinylcarbazole of 10 microns in thickness and a vacuum evaporated aluminum electrode of 0.3 cm<sup>2</sup> area. The applied electric voltage to said sandwich cell is DC 20 volts and the xenon lamp is used as a light source.

The new sensitizer according to the present invention has the following chemical formula:



wherein

$R_1$  is hydrogen or phenyl;

$R_2$  is hydrogen, phenyl or 4-methoxyphenyl, naphthyl, 2-methoxynaphthyl(1) or 4-methoxynaphthyl(1);

$R_3$  is hydrogen, methoxy, nitro or phenyl;

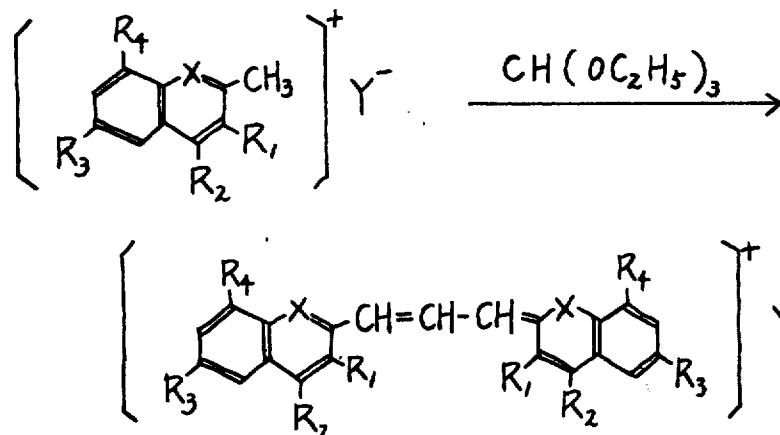
$R_4$  is hydrogen or methoxy;

X is oxygen or sulfur atom;

and  $Y^-$  is an anion radical such as perchlorate.

The compounds having the chemical formula above mentioned are called trimethine compounds.

The trimethine compounds are prepared by the following chemical equation:



wherein

$R_1$  is hydrogen or phenyl

$R_2$  is hydrogen, phenyl, 4-methoxyphenyl, naphthyl, 2-methoxynaphthyl(1) or 4-methoxynaphthyl(1);

$R_3$  is hydrogen, methoxy, nitro or phenyl;

$R_4$  is hydrogen or methoxy;

X is oxygen or sulfur atom;

and  $Y^-$  is an anion radical such as perchlorate.

Thus, 2-methylbenzopyrylium salt or 2-methylbenzothiaprylium salt is allowed to react with alkyl orthoformate in acetic anhydride at 40° to 130°C, preferably at 80° to 110°C.

Representative examples of 2-methylbenzopyrylium salts and 2-methylbenzothiaprylium salts are listed in Table 1.

Table 1

Compound	Name of Compound
a.	2-methyl-3-phenylbenzopyrylium perchlorate
b.	2-methyl-3-phenyl-8-methoxybenzopyrylium perchlorate
c.	2-methyl-3-phenyl-6-methoxybenzopyrylium perchlorate
d.	2-methyl-3-phenyl-6-nitrobenzopyrylium perchlorate
e.	2-methyl-4-p-methoxyphenylbenzopyrylium perchlorate
f.	2-methyl-3-phenyl-4-p-methoxyphenylbenzopyrylium perchlorate
g.	2-methyl-3,6-diphenyl-4-methoxyphenylbenzopyrylium perchlorate
h.	2-methyl-4-4'-methoxynaphthyl(1') benzopyrylium perchlorate
i.	2-methyl-3-phenyl-4-4'-methoxynaphthyl(1')

Table 1-Continued

Compound	Name of Compound
j.	benzopyrylium perchlorate
k.	2-methyl-3,6-diphenyl-4-4'-methoxynaphthyl(1') benzopyrylium perchlorate
l.	2-methyl-4-2'-methoxynaphthyl(1') benzopyrylium perchlorate
m.	2-methyl-3-phenyl-4-2'-methoxynaphthyl(1') benzopyrylium perchlorate
n.	2-methyl-3,6-diphenyl-4-2'-methoxynaphthyl(1') benzopyrylium perchlorate
o.	2-methyl-4-p-methoxyphenylbenzothiaprylium perchlorate
p.	2-methyl-3-phenyl-4-p-methoxyphenylbenzothiaprylium perchlorate
q.	2-methyl-4-4'-methoxynaphthyl(1') benzothiaprylium perchlorate
r.	2-methyl-3-phenyl-4-4'-methoxynaphthyl(1') benzothiaprylium perchlorate
s.	2-methyl-3,6-diphenyl-4-4'-methoxynaphthyl(1') benzothiaprylium perchlorate
t.	2-methyl-4-2'-methoxynaphthyl(1') benzothiaprylium perchlorate
u.	2-methyl-3-phenyl-4-2'-methoxynaphthyl(1') benzothiaprylium perchlorate
v.	2-methyl-3,6-diphenyl-4-2'-methoxynaphthyl(1') benzothiaprylium perchlorate
w.	2-methylbenzopyrylium chloroferrate
x.	2-methyl-3,6-diphenylbenzopyrylium perchlorate.

Table 2 lists additional information on the absorption maximum in dichloroethane and melting point of said salts listed in Table 1.

Table 2

Compound	Melting Point (°C)	Absorption Maximum in dichloroethane (m $\mu$ )
a.	177 ~ 179	585
b.	219 ~ 220	580
c.	206 ~ 208	375
d.	124 ~ 127	580
e.	129 ~ 130	442
f.	152 ~ 154	460
g.	226 ~ 227	475
h.	210 ~ 211	529
i.	181 ~ 184	516

Table 2—Continued

Compound	Melting Point (°C)	Absorption Maximum in dichloroethane (m $\mu$ )
j.	174 ~ 177	522
k.	236 ~ 237	540
l.	135 ~ 140	540
m.	181 ~ 185	527
n.	89 ~ 94	470
o.	212 ~ 213	482
p.	215 ~ 216	623
q.	220 ~ 222	561
r.	165 ~ 170	600
s.	180 ~ 185	579
t.	150 ~ 155	601
u.	163 ~ 165	603
v.	161 ~ 164	625
w.	118 ~ 119	565
x.	218 ~ 219	603

Table 3 shows representative examples of the benzopyranylidenepropenyl benzopyrylium salts and benzothiapyranylidenepropenyl benzothiapyrylium salts.

Table 3

Compound Number	Name of Compound
1.	2-[3'-(3''-phenyl-2''-benzopyranylidene)propenyl]-3-phenylbenzopyrylium perchlorate
2.	2-[3'-(3''-phenyl-8''-methoxy-2''-benzopyranylidene)propenyl]-3-phenyl-8-methoxybenzopyrylium perchlorate
3.	2-[3'-(3''-phenyl-6''-methoxy-2''-benzopyranylidene)propenyl]-3-phenyl-6-methoxybenzopyrylium perchlorate
4.	2-[3'-(3''-phenyl-6''-nitro-2''-benzopyranylidene)propenyl]-3-phenyl-6-nitrobenzopyrylium perchlorate
5.	2-[3'-(4''-p-methoxyphenyl-2''-benzopyranylidene)propenyl]-4-p-methoxyphenylbenzopyrylium perchlorate
6.	2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzopyranylidene)propenyl]-3-phenyl-4-p-methoxyphenylbenzopyrylium perchlorate
7.	2-[3'-(3'',6''-diphenyl-4''-p-methoxyphenyl-2''-benzopyranylidene)propenyl]-3,6-diphenyl-4-p-methoxyphenylbenzopyrylium perchlorate
8.	2-[3'-4''-(4'''-methoxynaphthyl(1'''))-2''-benzopyranylidene-propenyl]-4-(4'-methoxynaphthyl(1'))benzopyrylium perchlorate
9.	2-[3'-3''-phenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzopyranylidene propenyl]-3-phenyl-4-(4'-methoxynaphthyl(1'))benzopyrylium perchlorate
10.	2-[3'-3'',6''-diphenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzopyranylidene propenyl]-3,6-diphenyl-4-(4'-methoxynaphthyl(1'))benzopyrylium perchlorate
11.	2-[3'-4''-(2'''-methoxynaphthyl(1'''))-2''-benzopyranylidene-propenyl]-4-(2'-methoxynaphthyl(1'))benzopyrylium perchlorate
12.	2-[3'-3''-phenyl-4''-(2'''-methoxynaphthyl(1'''))-2''-benzopyranylidene propenyl]-3-phenyl-4-(2'-methoxynaphthyl(1'))benzopyrylium perchlorate
13.	2-[3'-3'',6''-diphenyl-4''-(2'''-methoxynaphthyl(1'''))-2''-benzopyranylidene propenyl]-3,6-diphenyl-4-(2'-methoxynaphthyl(1'))benzopyrylium perchlorate
14.	2-[3'-(4''-p-methoxyphenyl-2''-benzothiapyranylidene)propenyl]-4-p-methoxyphenylbenzothiapyrylium perchlorate
15.	2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzothiapyranylidene)propenyl]-3-phenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate
16.	2-[3'-(3'',6''-diphenyl-4''-p-methoxyphenyl-2''-benzothiapyranylidene)propenyl]-3,6-diphenyl-4-p-methoxyphenylbenzothiapyrylium perchlorate
17.	2-[3'-4''-(4'''-methoxynaphthyl(1'''))-2''-benzothiapyranylidene-propenyl]-4-(4'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
18.	2-[3'-3''-phenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzothiapyranylidene propenyl]-3-phenyl-4-(4'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
19.	2-[3'-3'',6''-diphenyl-4''-(4'''-methoxynaphthyl(1'''))-2''-benzothiapyranylidene propenyl]-3,6-diphenyl-4-(4'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
20.	2-[3'-4''-(2'''-methoxynaphthyl(1'''))benzothiapyranylidene-propenyl]-4-(2'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
21.	2-[3'-3''-phenyl-4''-(2'''-methoxynaphthyl(1'''))-2''-benzothiapyranylidene propenyl]-3-phenyl-4-(2'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
22.	2-[3'-3'',6''-diphenyl-4''-(2'''-methoxynaphthyl(1'''))-2''-benzothiapyranylidene propenyl]-3,6-diphenyl-4-(2'-methoxynaphthyl(1'))benzothiapyrylium perchlorate
23.	2-[3'-(2''-benzopyranylidene)propenyl]benzopyrylium perchlorate
24.	2-[3'-(3'',6''-diphenyl-2''-benzopyranylidene)propenyl]-3,6-diphenylbenzopyrylium perchlorate

Table 4 lists additional information on the absorption maximum in dichloroethane and melting point of the novel compounds according to the invention listed in Table 3.

Table 4

Compound Number	Melting Point (°C)	Absorption Maximum in dichloroethane (m $\mu$ )
1	253 ~ 255	646 and 706
2	280 ~ 282	652 and 715
3	283 ~ 285	679 and 745
4	194 ~ 198	645 and 704
5	150 ~ 153	667 and 727
6	241 ~ 243	664 and 726
7	>300	683 and 749
8	247 ~ 250	714
9	232 ~ 234	666 and 725
10	198 ~ 202	681 and 747
11	226 ~ 229	704
12	230 ~ 233	659 and 721
13	238 ~ 241	679 and 744
14	159 ~ 161	792
15	176 ~ 179	827

Table 4—Continued

Compound Number	Melting Point (°C)	Absorption Maximum in dichloroethane(m $\mu$ )
16	259 ~ 261	854
17	200 ~ 203	781
18	219 ~ 222	830
19	235 ~ 238	857
20	232 ~ 235	777
21	184 ~ 186	818
22	220 ~ 223	850
23	163 ~ 168	690
24	>300	670 and 734

The following description will explain a practical method for making the trimethine compounds with reference to 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 preparative methods for various compounds according to the invention:

1. 2-[3'-(3''-phenyl-2''-benzopyranylidene)propenyl]-3-phenylbenzopyrylium perchlorate (compound No. 1). 16 Grams of 2-methyl-3-phenylbenzopyrylium perchlorate is dissolved in 200 milliliters of acetic anhydride to a solution. After adding 19 grams of ethyl orthoformate, the solution is stirred for 15 minutes at 100°C. After cooling to room temperature, the solution is slowly poured into 2 liters of 10 percent perchloric acid to obtain a precipitate. The precipitate is filtered off, dried, washed with 300 milliliters of acetonitrile and dried again to obtain 7 grams of lustrous crystals having a melting point of 253° to 255°C.

2. 2-[3'-(3''-phenyl-4''-p-methoxyphenyl-2''-benzothiapyranylidene)propenyl]-3-phenyl-4-p-methoxyphenyl-benzothiapyrylium perchlorate (compound No. 15)

4.4 Grams of 2-methyl-3-phenyl-4-p-methoxyphenyl-benzothiapyrylium perchlorate (melting point 212° to 213°C) which is obtained by the Grignard reaction of 2-methyl-3-phenylbenzothiachromone and p-methoxyphenyl magnesium bromide, are dissolved in 80 milliliters of acetic anhydride to obtain a solution. After adding 3.8 grams of ethyl orthoformate, the solution is stirred for 15 minutes at 100°C. After cooling to the room temperature, the solution is slowly poured into 400 milliliters of 10 percent perchloric acid to obtain a precipitate. The precipitate is filtered off, dried and reprecipitated with dichloroethane-ethyl ether to obtain 6 grams of fine crystals having a melting point of 176° to 179°C.

It has been discovered according to the invention the compounds listed in Table 3 are sensitizers which can improve the photoconductivity and the spectrum characteristics of photoconductive polymers such as poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyacenaphthylene, etc. These polymers, except brominated poly-N-vinylcarbazole, are prepared by 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 are 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 and is poured into methanol to obtain a white

polymer. The 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. 39.44 weight percent of the monobromo substituted product from poly-N-vinylcarbazole. This indicates that the polymer obtained is a monobromo substituted 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 3 is dissolved in a suitable solvent, such as dichloroethane, methylene chloride, chloroform, or a combination thereof, and is added to the solution of the photoconductive polymer described above. The preferable amount of the sensitizer added is from 0.01 to 5.0 weight parts in connection with 100 weight parts of the photoconductive polymer. Advantageously, the amount thereof is from 0.1 to 2.0 weight parts in connection with 100 weight parts of the photoconductive polymer.

For the preparation of the photoconductive layer, a said solution of the photoconductive polymer and the sensitizer in a suitable solvent is applied to the suitable support such as the electroconductive support in per se usual manner, for example, by spraying, by means of blade coating, by means of whirler coating, etc., and then dried so as to produce a homogeneous transparent photoconductive layer on the support. Operable solvents are benzene, toluene, chlorobenzene, dioxane, methylene chloride, 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 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 e.g. metal plate or glass plate having an electrically conductive coating, plastic plate or foil or film made of electrically conductive resin or coated with evaporated thin metal layer or covered with cuprous iodide conductive layer. The transparent support can produce a transparent photoconductive or electrophotographic plate, foil or film.

The reproduction of images by the electrophotographic method is carried out as follows: when the photoconductive layer has been charged by means of a corona discharge apparatus, the sensitized layer with the support is exposed to light under a master and is then dusted over in a per se 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.

This invention is still further illustrated with references to the following illustrative examples.

#### EXAMPLE 1

1 Gram of polyacenaphthylene and 0.6 gram of, as a plasticizer, chlorinated diphenyl (commercially avail-



able as "Kanechlor"), are dissolved in 8 milliliters of chlorobenzene. To the solution are added 0.5 milliliters of dichloroethane containing 0.006 gram of a sensitizer corresponding to compound number listed in Table 3. The solution is applied to an aluminum plate by means of whirler coating and is dried to form a layer of 7 microns in thickness. After said aluminum plate provided with the layer is charged negatively 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 exposed to a 100W tungsten lamp at an illumination of 50 lux, 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 low melting point polystyrene, colophony and carbon black. The toner is mixed with a carrier substance such 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 5, there are shown the sensitivity which is defined as a half-decay-exposure in lux-second units, said half-decay-exposure is the exposure to reduce a surface potential of the photoconductive layer to a half of the surface potential in the dark. The smaller half-decay-exposure represents a higher sensitivity.

Table 5

Compound No.	Half-decay Exposure $E_{50}$ (lux.sec)
2	380
7	270
8	150
11	160
18	60
22	410
24	160

## EXAMPLE 2

1 Gram of poly-N-vinylcarbazole, 0.5 gram of chlorinated diphenyl (commercially available as "Kanechlor") and 0.006 gram of a sensitizer, corresponding to compound number listed in Table 3, are dissolved in 10 milliliters of dichloroethane to obtain a solution. The solution is applied to a polyester film (0.1 mm in thickness) having a cuprous iodide transparent conductive layer by means of blade coating and is dried to form a layer of 10 microns in thickness. An electrophotographic image is produced in the same way as that described in Example 1. In Table 6, there are shown the sensitivity as the half-decay exposure in lux-second units.

Table 6

Compound No.	Half-decay Exposure $E_{50}$ (lux.sec)
2	8.3
3	10.1
5	8.8
7	6.2
8	6.9
11	8.4
22	16.0
23	20.0
24	7.0

It is clear from Table 6 that the novel sensitizers improve the photoconductivity of poly-N-vinylcarbazole.

## EXAMPLE 3

1 Gram of brominated poly-N-vinylcarbazole (monobromosubstituted product), 0.5 grams of polycarbonate resin (commercially available as "Panlite-C"), 0.3 gram of chlorinated diphenyl (commercially available as "Kanechlor") and 0.002 gram of sensitizer listed in Table 3 are dissolved in a mixed-solvent of 8 milliliters of chlorobenzene and 2 milliliters of dichloroethane. This solution is applied to a polyester film (0.1 mm in thickness) having a cuprous iodide transparent conductive layer by means of a blade coating and dried to form a layer of 14 microns in thickness. On this support, an electrophotographic image is produced in the same way as that described in Example 1. Table 7 shows the sensitivity as the half-decay exposure in lux-second units.

Table 7

Compound No.	Half-decay Exposure $E_{50}$ (lux.sec)
1	4.7
2	6.1
3	7.8
4	4.7
5	7.5
6	15.0
7	4.0
8	11.0
9	38.0
10	17.0
11	7.8
12	10.0
13	10.0
14	6.4
15	15.0
16	9.5
17	11.0
18	8.0
19	10.0
20	24.0
21	18.0
22	18.0
23	15.0
24	4.6

It is clear from Table 7 and FIGS. 5 to 8 that the novel sensitizers improve the photoconductivity and the spectrum characteristics of brominated poly-N-vinylcarbazole.

## EXAMPLE 4

A dichloroethane solution containing poly-N-vinylcarbazole and a sensitizer listed in Table 3 is applied to a glass plate having an electrically conducting layer (commercially available as "NESA GLASS" and the solvent is evaporated to obtain a sensitized photoconductive layer of 10 microns in thickness of poly-N-vinylcarbazole. The concentration of the sensitizer in poly-N-vinylcarbazole is 0.2 mole percent.

FIG. 2 to FIG. 4 show the illustrations of the absorption spectra of the sensitized photoconductive films.

Then, aluminum is evaporated onto the parallel face of the layer as electrode to obtain a photoconductor cell (sandwich type cell). Area of the aluminum electrode is  $0.03\text{cm}^2$ . The cell is illuminated by a light which has a peak at an absorption maximum of the sensitizer. The light is obtained from a xenon lamp with a saturated  $\text{CuSO}_4$  solution and a colored glass.

The photocurrent increases almost linearly with applied electric field up to  $2 \times 10^4$  volt/cm. Photocurrent is proportional to the intensity of the light.

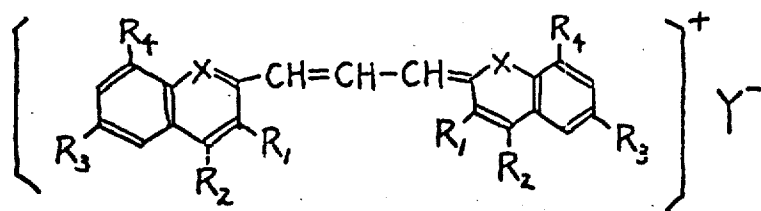
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The spectral response of the photocurrent is measured in a range from 400mμ to 1000mμ with the xenon lamp and the monochromator (Hitachi type EPU-2A). FIG. 9 shows the illustration of the spectral response of the photoconductor cell.

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.

What we claim is:

1. An organic photoconductive layer comprising a combination of an organic photoconductor and a sensitizer having the following chemical formula.



wherein

- R<sub>1</sub> is hydrogen or phenyl;
- R<sub>2</sub> is hydrogen, phenyl, 4-methoxyphenyl, naphthyl, 2-methoxynaphthyl(1) or 4-methoxynaphthyl(1);
- R<sub>3</sub> is hydrogen, methoxy, nitro or phenyl;
- R<sub>4</sub> is hydrogen or methoxy;
- X is oxygen or sulfur atom;
- and Y<sup>-</sup> is a perchlorate radical, said combination comprising 100 weight parts of an organic photo-

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conductor and 0.01 to 5.0 weight parts of a sensitizer.

- 2. An electrophotographic material comprising an electrically conductive support layer and photoconductive layer, the latter comprising a combination of photoconductive polymer and a sensitizer having the chemical formula according to claim 1, said combination comprising 100 weight parts of an organic photoconductor and 0.01 to 5.0 weight parts of a sensitizer.
- 3. An electrophotographic material according to claim 2, wherein said photoconductive polymer is one member from the group consisting of poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole and polyacenaphthylene.
- 4. A transparent photoconductive layer comprising a

- 25 combination of a photoconductive polymer and a sensitizer having the chemical formula according to claim 1, said combination comprising 100 weight parts of an organic photo conductor and 0.01 to 5.0 weight parts of a sensitizer.
- 30 5. A transparent photoconductive layer according to claim 4, wherein said photoconductive polymer is one member from the group consisting of poly-N-vinylcarbazole and brominated poly-N-vinylcarbazole.

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