# [54] ELECTROPHOTOGRAPHIC MATERIAL CONTAINING SENSITIZERS

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[22] Filed: Aug. 7, 1974

[21] Appl. No.: 495,520

### Related U.S. Patent Documents

#### Reissue of:

[64] Patent No.: 3,712,811 Issued: Jan. 23, 1973 Appl. No.: 121,508 Filed: Mar. 5, 1971

#### [30] Foreign Application Priority Data Mar. 13, 1970 Japan......

Mar. 13, 1970	Japan	45-21766
Mar. 13, 1970	Japan	45-21767

[58] Field of Search ....... 96/1.5, 1.6, 1.7; 252/501; 260/327, 345.2

## [56] References Cited UNITED STATES PATENTS

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Primary Examiner—Norman G. Torchin Assistant Examiner—Judson R. Hightower Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

#### [57] ABSTRACT

An electrophotographic material is provided herein which comprises a conductive support layer and a photoconductive insulating layer, the latter layer comprising a photoconductive polymeric compound such as poly-N-vinylcarbazole, and a sensitizer having the following general formula

wherein

B represents a radical selected from the group consisting of

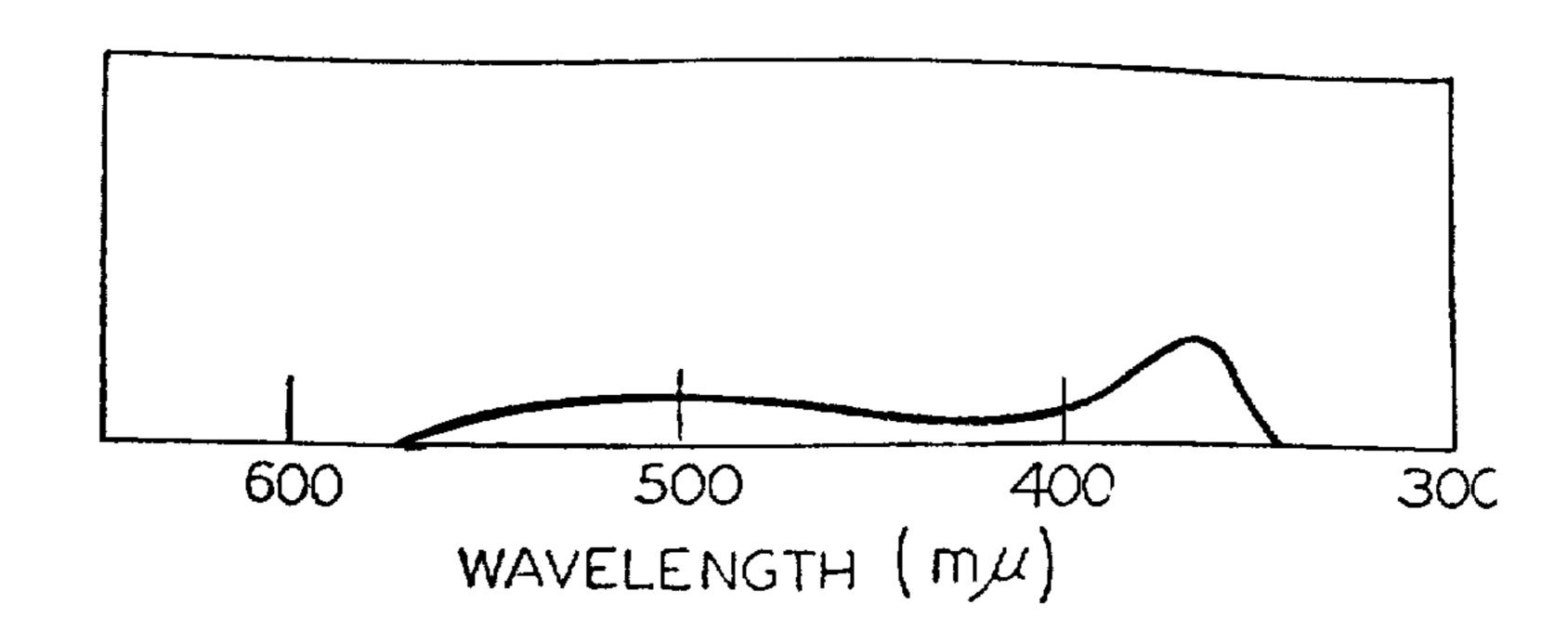
$$R_7$$
 $R_5$ 
 $R_6$ 
and
 $R_8$ 
 $OCH_3$ 

$$\bigcap_{R_0}^{X} \text{ and } \bigcap_{R_0}^{O}$$

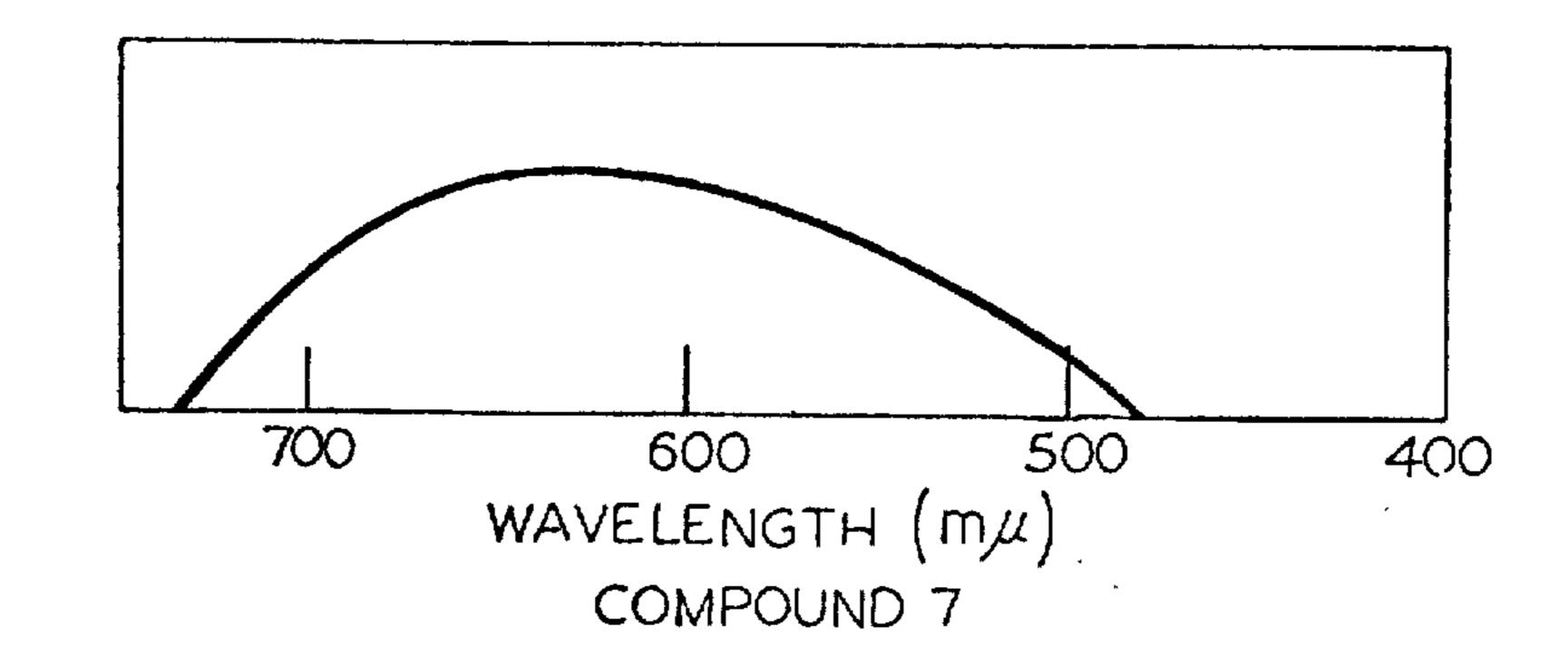
Compounds falling under the latter general formula include such compounds as 2-phenyl-4-[(2'-phenyl-4'-benzopyranylidene) benzyl]-benzopyrylium perchlorate and 2,3-phenyl-4-[(2'-phenyl 4'-benzopyranylidene)benzyl]-6-methylbenzopyrylium perchlorate.

#### 3 Claims, 9 Drawing Figures

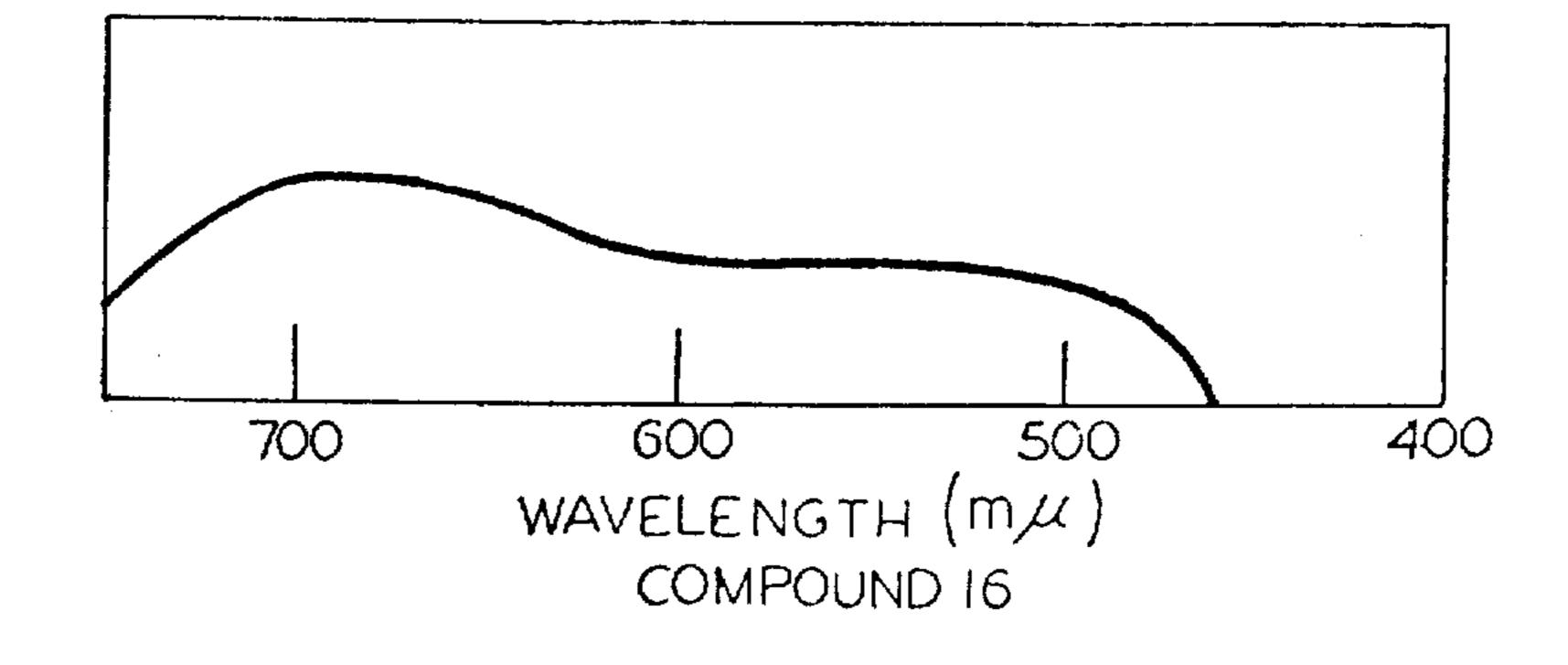
FIG.1

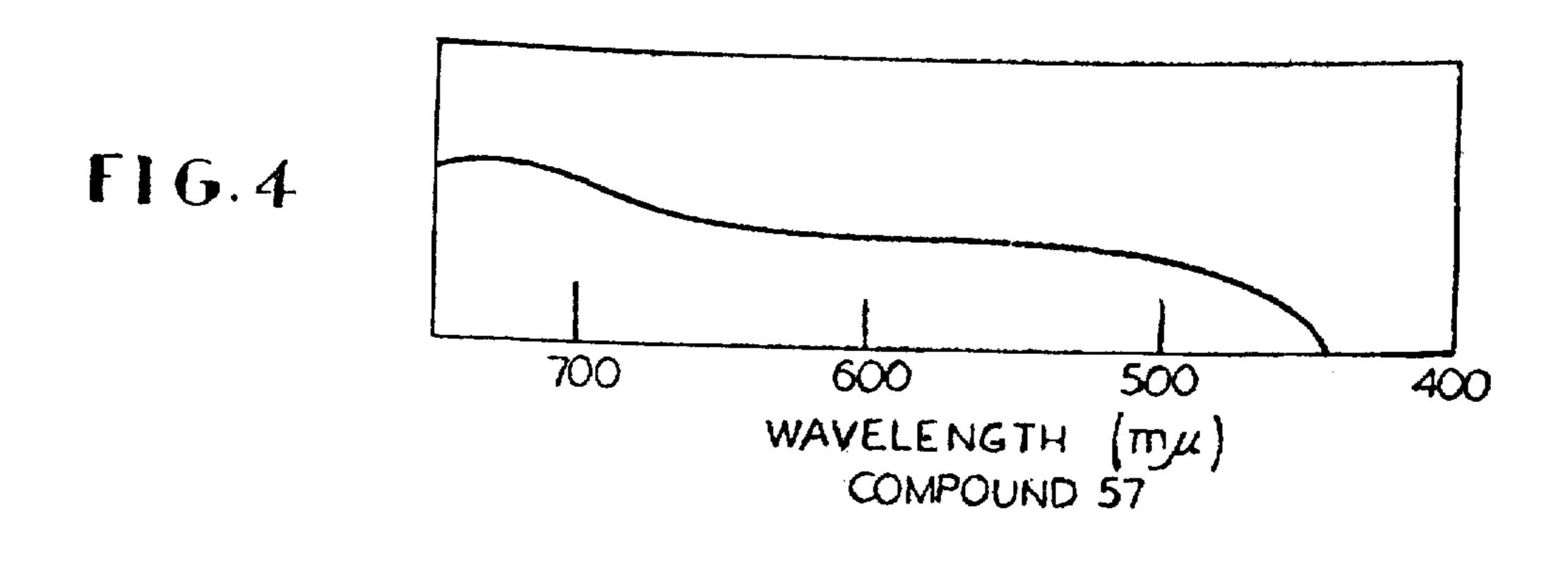


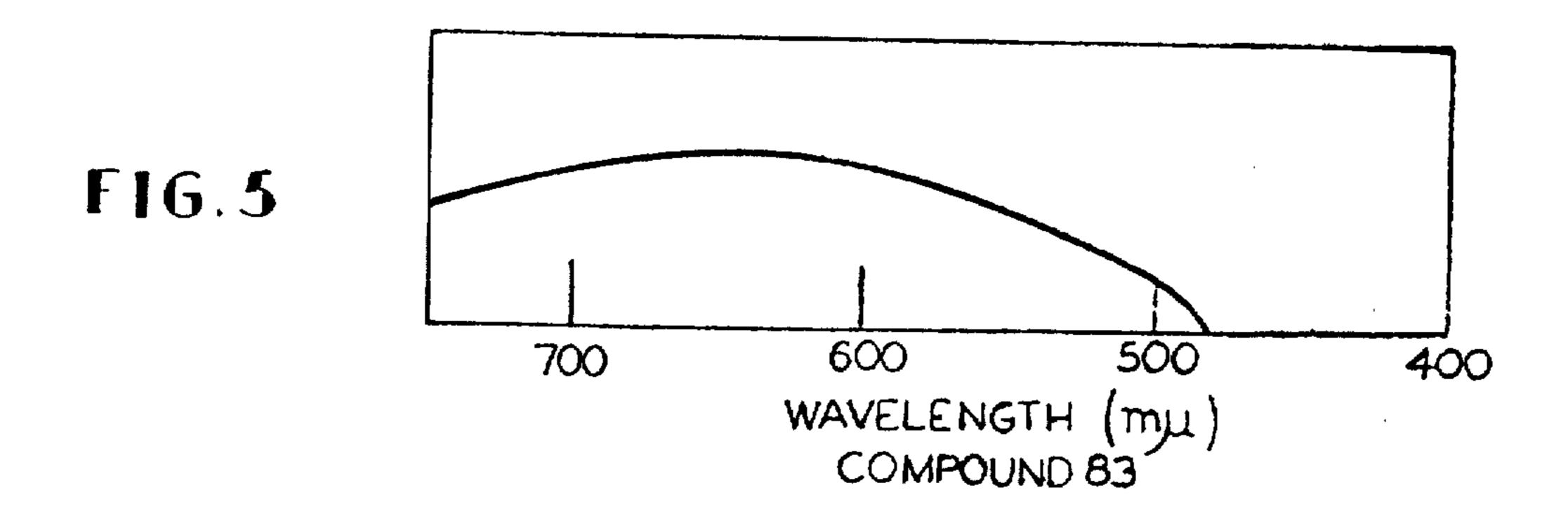
F16.2

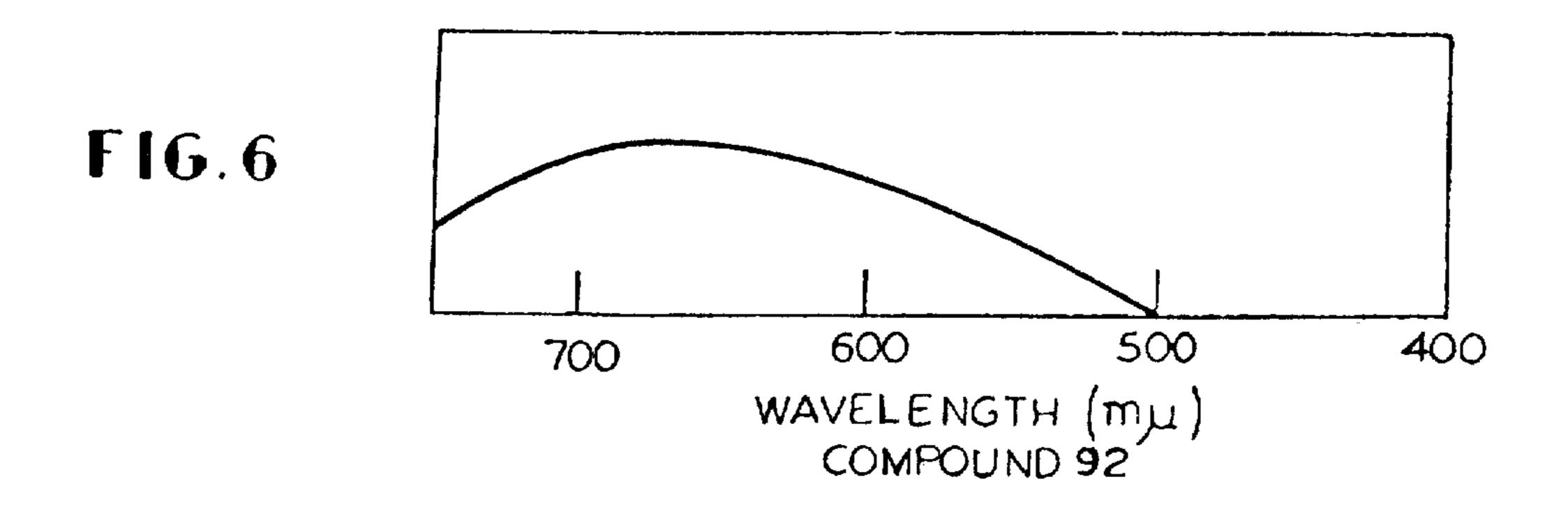


F 1 G.3

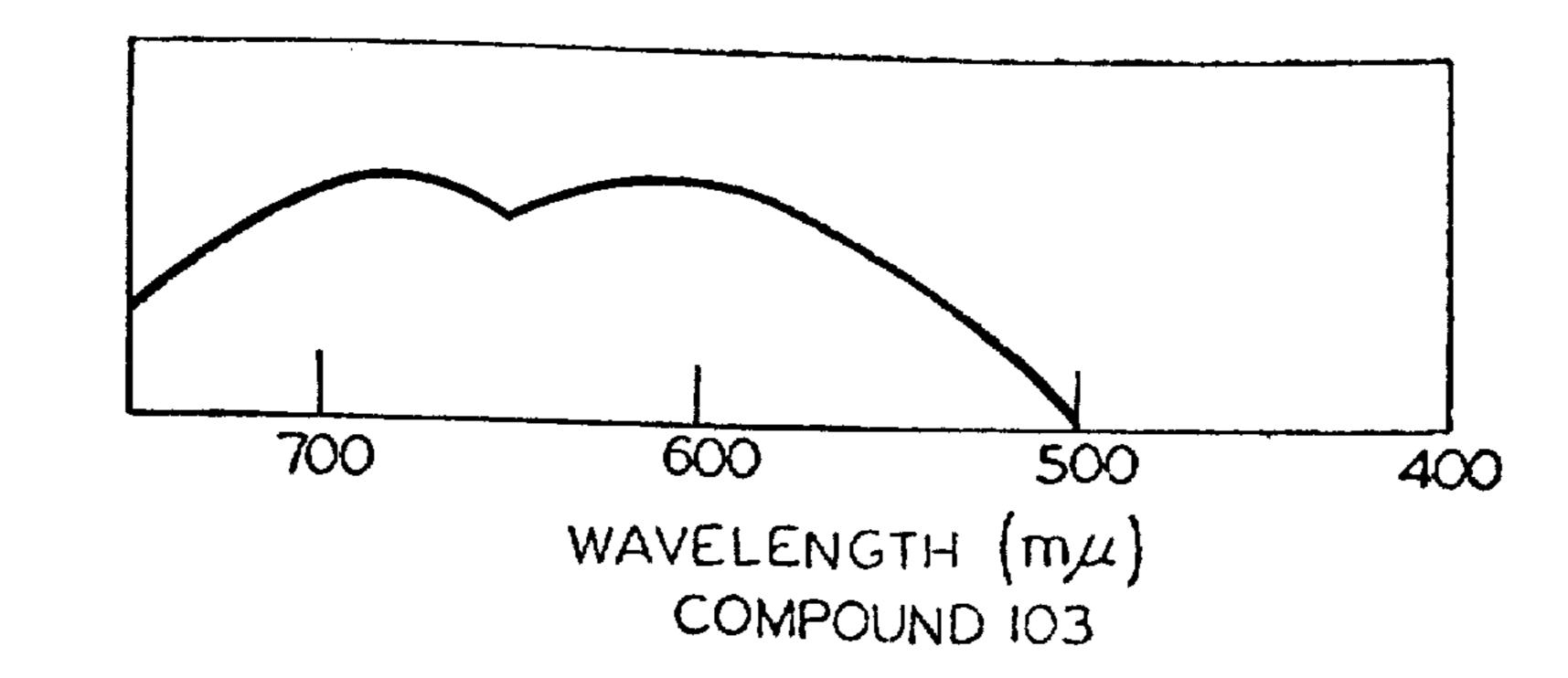




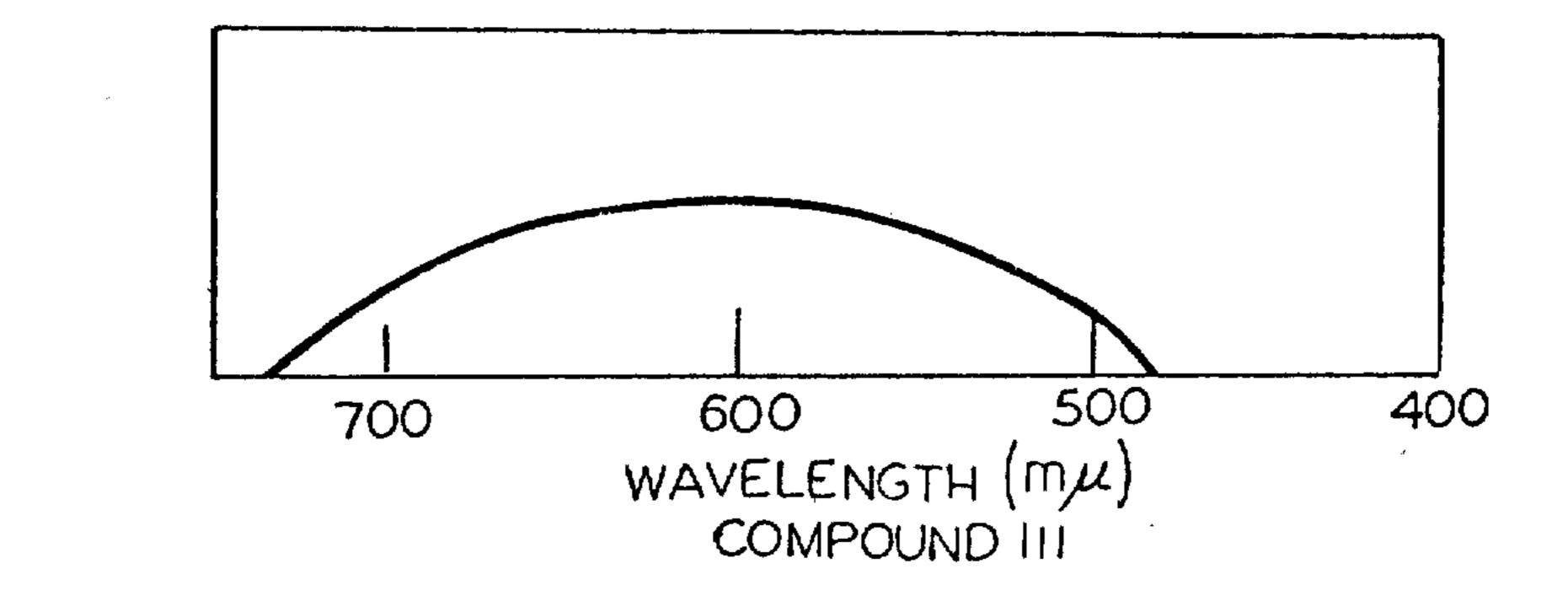




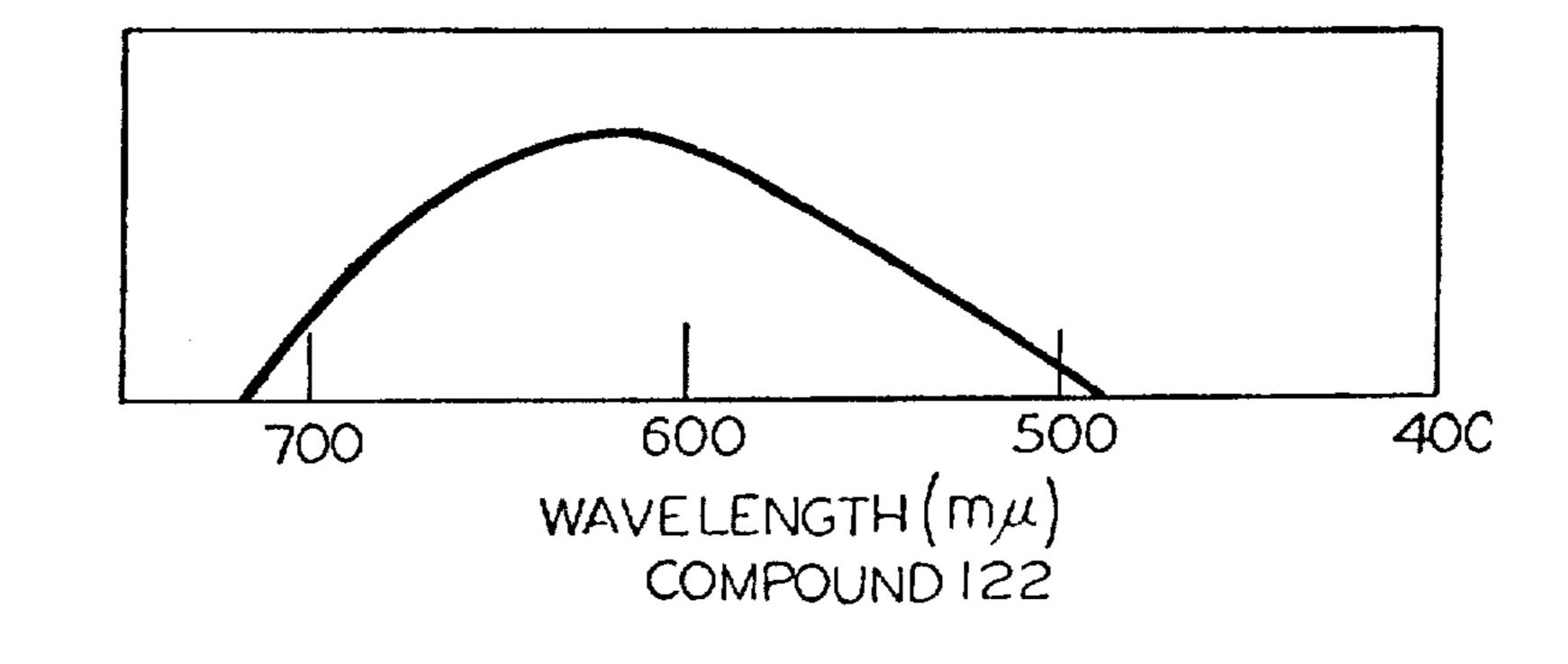
F16.7



F16.8



F16.9



### ELECTROPHOTOGRAPHIC MATERIAL **CONTAINING SENSITIZERS**

Matter enclosed in heavy brackets [ ] appears in the 5 original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This invention relates to novel light-sensitive layers and more particularly to electrophotographic light-sensitive polymer layers.

Various light-sensitive layers are well known in the ments, drawings, transparencies, etc. These layers contain organic photoconductive compounds, such as poly-N-vinylcarbazole, brominated poly-N-vinylcarbazoles, polyacenaphthylene, etc. These layers are non-conductors of electricity before exposure and be- 20 come electrical conductors upon exposure.

It is necessary for the electrophotographic art that the photoconductive material has a high photoconductivity in the long wavelength region of the visible spectrum. Such a photoconductive material makes it possi- 25 ble for the electrophotograph 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 the short wavelength 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 photoconductivity and spectrum characteristics of the above photoconductive compounds. Conventional sensitizers are dyestuff compounds, such as triarylmethane dyes, xanthene dyes, triazine dyes or acridine dyes, but the conventional sensitizers are not 40 entirely satisfactory to improve the photoconductivity and the spectrum characteristics of the available photoconductive compounds.

In addition to the high photoconductivity and spectrum characteristics sensitive to visible light, the elec- 45 trophotographic 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 50 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 wavelength 55 region of the visible spectrum.

Another object of the invention is to provide electrophotographic materials having a high electric resistance in the dark.

These and other objects are accomplished by adding 60 a new sensitizer shown hereinafter to a photoconductive polymeric compound such as poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole or polyacenaphthylene, 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 an unsensitized solution of 10 weight percent of brominated poly-Nvinylcarbazole in chlorobenzene.

FIG. 2 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-( $\alpha$ phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-ben-

zopyranylidene)-methyl]benzopyrylium perchlorate, the 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 elecelectrophotographic art for making copies of docu- 15 trophotographic material coated with a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-styryl-3-phenyl-4-[(2'-styryl-4'-benzopyranylidene)methyl]-6-methylbenzopyrylium perchlorate, the 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 a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-pmethoxystyryl-4-[2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate, the 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 a solution containing 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-pmethoxystyryl-4-[(2'-phenyl-4'-benzothiperchlorate. opyranylidene)-methyl]benzopyrylium the 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 electrophotograph material coated with a solution containing 10 weight percent of brominated poly-N-vinyl carbazole sensitized with 0.04 weight percent of 2-[(2'phenyl-4'-benzopyranylidene)methyl]3-phenylbenzopyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a solvent of four 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-[(4'benzothiopyranylidene)methyl]-3-phenylben-

zopyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a 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-[(2'- $\alpha$ -phenyl-p-methoxystyryl-4'-benzopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate, the brominated poly-N-vinylcarbazole being dissolved in a solvent of four weight parts of chlorobenzene and one weight part of dichloroethane.

FIG. 9 represents the wedge spectrogram for an electrophotographic material coated with a solution con-

35

55

60

3

aining 10 weight percent of brominated poly-N-vinylcarbazole sensitized with 0.04 weight percent of 2-[(2'phenyl-4'-benzothiopyranylidene)methyl]-3-phenylpenzopyrylium perchlorate, the brominated poly-Nvinylcarbazole being dissolved in a solvent of four 5 weight parts of chlorobenzene and one weight part of lichloroethane.

The new sensitizer, according to the present invenion has the following formula:

$$\begin{bmatrix}
X & R_1 \\
R_3 & C-R_4
\end{bmatrix}$$
Anion
15

here B represents a radical selected from the group 20 onsisting of,

$$R_7$$
 $R_6$ 
 $R_6$ 
 $R_8$ 
 $OCH_3$ 
 $R_8$ 
 $OCH_3$ 

$$\mathbb{R}_{7} \stackrel{O}{\longrightarrow} \mathbb{R}_{5}$$

$$\bigcap_{R_9}^{X} \bigcap_{R_9}^{A}$$

- is hydrogen, phenyl or an ethenyl or an ethenyl radical selected from the group consisting of styryl, pmethoxystyryl, 3,4-dimethoxystyryl,  $\alpha$ -phenylstyryl,  $\beta$ -furyl( $\alpha'$ ) ethenyl and  $\alpha$ -phenyl- $\beta$ -furyl( $\alpha'$ )-ethenyl;
- 2 is hydrogen or phenyl;
- 3 is hydrogen, methyl or phenyl;
- is hydrogen or phenyl;
- is hydrogen, phenyl or an ethenyl radical selected from the group consisting of styryl, p-methoxystyryl, 3,4-dimethoxystyryl,  $\alpha$ -phenyl-p-methoxystyryl,  $\beta$ furyl( $\alpha'$ )ethenyl and  $\alpha$ -phenyl- $\beta$ -furyl( $\alpha'$ )ethenyl;
- 6 is hydrogen or phenyl;
- 7 is hydrogen, methyl or phenyl;
- 8 is hydrogen or phenyl;
- B is hydrogen or p-methoxyphenyl;
- e anion is anionic function selected from the group onsisting of perchlorate, fluoroborate, chloroferrate, 65 ilorozincate and nitrate; and
- is oxygen or sulfur atom.
- The sensitizers having the formula above mentioned e prepared by the following chemical equations A or

Equation A  $\begin{bmatrix}
R_1 \\
R_2
\end{bmatrix}
\xrightarrow{R_2}
\xrightarrow{R_2}$ OCH<sub>3</sub>
(I)

$$\left(\begin{array}{c}
R_7 \\
R_7
\end{array}\right) \begin{array}{c}
R_5 \\
R_6 \\
CH_2 \\
R_4
\end{array} (II)$$
Anion

$$\begin{array}{c}
 & \times & \times & \times \\
 & \times & \times & \times$$

Equation B  $\begin{pmatrix}
 & X & R_1 \\
 & R_2 & \\
 & OCH_3
\end{pmatrix}
+ NO_2 - +$ 

(III)

$$\begin{pmatrix} CH_3 \\ R_8 \end{pmatrix}$$
Anion

 $\begin{array}{c}
(IV) \\
R_3 \\
R_8 \\
CH \\
R_2 \\
Anion
\end{array}$ (V)

In the case of Equation A, 4-[(4'-ben-zopyranylidene)-methyl]benzopyrylium derivative (III) is obtained by an addition reaction of 4-methox-ybenzopyrylium o-nitrobenzene sulfonate (I) with a benzopyrylium salt (II) in an acetic anhydride solution. The benzopyrylium salt has an active methyl or methylene radical.

In the case of Equation B, 2-[(4'-ben-zopyranylidene)-methyl]benzopyrylium derivative (V) is obtained by an addition reaction of 4-methoxyben-

zopyrylium o-nitrobenzene sulfonate (I) with a benzopyrylium salt (IV) in an acetic anhydride solution. The benzopyrylium salt has an active methyl radical.

In both cases, methyl 2,4-dinitrobenzene sulfonate, 5 dimethyl sulfate or methyl iodide can be used instead of methyl o-nitrobenzene sulfonate.

Representative examples of the benzopyranylidenemethylbenzopyrylium salts and benzothiopyranylidene-methylbenzopyrylium salts according 10 to the invention are listed in Table I.

	Table 1	
Com- pound Number	Name of Compound	15
<u> </u>		
1.	2-phenyl-4-[(2'-phenyl-4'-benzopyranylidene)benzyl]- benzopyrylium perchlorate	
2.	2,3-diphenyl-4-[(2'-phenyl-4'-benzopyranylidene)-ben-	
1	zyl]-6-methylbenzopyrylium perchlorate 2.3-diphenyl-4-1(2'-phenyl-4'-benzopyranylidene).	
3.	2,3-diphenyl-4-[(2'-phenyl-4'-benzopyranylidene)- methyl]-6-methylbenzopyrylium perchlorate	20
4.	2,3-diphenyl-4-[(2'-phenyl-4'-benzopyranylidene)-	
5.	methyl]-6-phenylbenzopyrylium perchlorate 2-p-methoxystyryl-4-[(2'-phenyl-4'-benzopyranylidene)-	
	methyl]benzopyrylium perchlorate	
6.	2-β-furyl(α')ethenyl-4-[(2'-phenyl-4'-benzopyranylidene-	
7.	methyl]benzopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-ben-	25
•	zopyranylidene)methyl]benzopyrylium perchlorate	
8.	2-styryl-3-phenyl-4-[(2'-phenyl-4'-benzopyranylidene)- methyl]-6-methylbenzopyrylium perchlorate	
9.	2-p-methoxystyryl-3-phenyl-4-{(2'-phenyl-4'-ben-	
	zopyranylidene)methyl]-6-methylbenzopyrylium	
10.	perchlorate 9-[(2'-phenyl-4'-benzopyranylidene)methyl]xanthylium	20
	perchlorate	30
11.	$2-\beta$ -furyl( $\alpha'$ )ethenyl-3-phenyl-4-[(2'-phenyl-4'-ben-	
	zopyranylidene)methyl]-6-methylbenzopyrylium perchlorate	
12.	2,3-diphenyl-4-[(2'-styryl-4'-benzopyranylidene)benzyl]-	
13.	6-methylbenzopyrylium perchlorate 2-phenyl-4-[(2'-styryl-4'-benzopyranylidene)benzyl]ben-	
13.	z-pitetiyi-4-[(2 -styryi-4 -betizopyranyildene/betizyi beti- zopyrylium perchlorate	35
14.	2,3-diphenyl-4-[(2'-styryl-4'-benzopyranylidene)methyl]-	
15.	6-methylbenzopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-styryl-4'-ben-	
1.5.	zopyranylidene)methyl]benzopyrylium perchlorate	
16.	2-styryl-3-phenyl-4-[(2'-styryl-4'-benzopyranylidene)me-	
17.	thyl]-6-methylbenzopyrylium perchlorate 9-{(2'-styryl-4'-benzopyranylidene)methyl]xanthylium	40
1,.	perchiorate	
18.	2-p-methoxystyryl-3-phenyl-4-[(2'-styryl-4'	
	-benzopyranylidene)methyl]-6-methylbenzopyrylium perchlorate	
19.	2,3-diphenyl-4-[(4'-benzopyranylidene)benzyl]-ben-	
20.	zopyrylium perchlorate 2-phenyl-4-[(4'-benzopyranylidene)benzyl]benzopyrylium	45
20.	perchlorate	
21.	2,3-diphenyl-4-[(4'-benzopyranylidene)methyl]-6-methyl-	
22.	benzopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(4'-benzopyranylidene)-	
22.	methyl]benzopyrylium perchlorate	
23.	2-styryl-3-phenyl-4-[(4'-benzopyranylidene)methyl]-6-	50
24.	methylbenzopyrylium perchlorate 2-p-methoxystyryl-3-phenyl-4-{(4'-benzopyranylidene)-	
	methyl]-6-methylbenzopyrylium perchlorate	
25. 26.	9-[(4'-benzopyranylidene)methyl]xanthylium perchlorate 2-p-methoxystyryl-4-[(4'-benzopyranylidene)methyl]-ben-	
20.	zopyrylium perchlorate	
27.	2-p-methoxystyryl-4-[(2'-p-methoxystyryl-4'-ben-	55
28.	zopyranylidene)methyl]benzopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-p-methoxystyryl-4'-	
20.	benzopyranylidene)methyl]benzopyrylium perchlorate	
29.	2-styryl-3-phenyl-4-[(2'-p-methoxystyryl-4'-ben-	
	zopyranylidene)methyl]-6-methylbenzopyrylium perchlorate	
30.	2,3-diphenyl-4-[(2'-p-methoxystyryl-4'-ben-	60
	zopyranylidene)-methyl]-6-methylbenzopyrylium	•
31.	perchlorate 2,3-diphenyl-4-[(2'-p-methoxystyryl-4'-ben-	
	zopyranylidene)benzyl]-6-methylbenzopyrylium	
2.7	perchiorate  2 phonul 4 (42' n methoxyetyrul 4' henzonyranylidene).	
32.	2-phenyl-4-[(2'-p-methoxystyryl-4'-benzopyranylidene)- benzyl]benzopyrylium perchlorate	Z i
33.	9-[(2'-p-methoxystyryl-4'-benzopyranylidene)methyl]-	65
34.	xanthylium perchlorate 2-p-methoxystyryl-4-[(4'-benzothiopyranylidene)methyl]-	
J <b>₹</b> .	benzopyrylium perchlorate	
35.	2-(α-phenyl-p-methoxystyryl)-4-[(4'-benzothi-	
36.	opyranylidene)-methyl]benzopyrylium perchlorate 2-styryl-3-phenyl-4-[(4'-benzothiopyranylidene)methyl]-	
	6-methylbenzopyrylium perchlorate	
37.	2,3-diphenyl-4-[(4'-benzothiopyranylidene)methyl]-6- methylbenzonyrylium perchlorate	
	meinvioenzonviviiiiii nerchaltale	

	Table 1-continued
Com- pound Number	Name of Compound
38.	2,3-diphenyl-4-[ (4'-benzothiopyranylidene)benzyl]-6-methylben-
39.	zopyrylium perchlorate 2-phenyl-4-[(4'-benzothiopyranylidene)benzyl]ben- zopyrylium perchlorate
40.	9-[(4'-benzothiopyranylidene)methyl xanthylium perchlorate.
41.	2-p-methoxystyryl-3-phenyl-4-{(4'-benzothi- opyranylidene)-methyl]-6-methylbenzopyrylium perchlorate
42.	2-p-methoxystyryl-4-{(2'-3'',4''-dimethoxystyryl-4'-ben-zopyranylidene)methyl]benzopyrylium perchlorate
43.	2-styryl-3-phenyl-4-[(2'-3'',4''-dimethoxystyryl-4'-ben-zopyranylidene)methyl]-6-methylbenzopyrylium perchlorate
44.	9-[(2'-3'',4"-dimethoxystyryl-4'-benzopyranylidene)- methyl]xanthylium perchlorate
45.	2-phenyl-4-[(2'-β-furyl(α')ethenyl-4'-benzopyranylidene)- benzyl]benzopyrylium perchlorate
46.	2,3-diphenyl-4-[(2'-\beta-furyl(\alpha')ethenyl-4'-ben- zopyranylidene)benzyl]-6-methylbenzopyrylium perchlorate
47.	2,3-diphenyl-4-[(2'-β-furyl(α')ethenyl-4'-ben- zopyranylidene)methyl]-6-methylbenzopyrylium perchlorate
48.	2-p-methoxystyryl-4-[(2'-β-furyl(α')ethenyl-4'-ben- zopyranylidene)methyl benzopyrylium perchlorate
49. 50	2-(α-phenyl-p-methoxystyryl)-4-((2'-β-furyl(α')ethenyl- 4'-benzopyranylidene)methyl]benzopyrylium perchlorate
50. 51.	9-[(2'-β-furyl(α')ethenyl-4'-benzopyranylidene)methyl]- xanthylium perchlorate 2-phenyl-4-[(2'-α-phenylstyryl-4'-benzopyranylidene)-
52.	benzyl]benzopyrylium perchlorate 2-p-methoxystyryl-4-{(2'-α-phenylstyryl-4'-ben-
53.	zopyranylidene)methyl]benzopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-α-phenylstyryl-4'-
54.	benzopyranylidene)methyl]benzopyrylium perchlorate 2-phenyl-4-[(2'-α-phenyl-p-methoxystyryl-4'-ben-
55.	zopyranylidene)benzyl]benzopyrylium perchlorate 2,3-diphenyl-4-[(2'-α-phenyl-p-methoxystyryl-4'-ben- zopyranylidene)benzyl] -6-methylbenzopyrylium
56.	perchlorate 2,3-diphenyl-4-{(2'-α-phenyl-p-methoxystyryl-4'-ben- zopyranylidene)methyl}-6-methylbenzopyrylium perchlorate
57.	2-p-methoxystyryl-4-[(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate
58.	2-(α-phenyl-p-methoxystyryl)-4-[(2'-α-phenyl-p-methoxy- styryl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate
59.	9-[(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)- methyl]xanthylium perchlorate
60. 61.	2-p-methoxystyryl-4-[(2'-α-phenyl-β-furyl(α')ethenyl-4'- benzopyranylidene)methyl benzopyrylium perchlorate
62.	9-[(2'-α-phenyl-β-furyl(α')ethenyl-4'-ben- zopyranylidene)methyl]xanthylium perchlorate 2-phenyl-4-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl-4'-
63.	benzopyranylidene)benzyl]benzopyrylium perchlorate 2,3-diphenyl-4-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl- 4'-benzopyranylidene)benzyl]-6-methylbenzopyrylium
64.	perchlorate 2,3-diphenyl-4-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl- 4'-benzopyranylidene)methyl]-6-methylbenzopyrylium
65.	perchlorate 2-p-methoxystyryl-4-[(2'-p-methoxystyryl-3'-phenyl-6'- methyl-4'-benzopyranylidene)methyl]benzopyrylium
66.	perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-p-methoxystyryl-3'- phenyl-6'-methyl-4'-benzopyranylidene)methyl]ben-
67.	zopyrylium perchlorate 9-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl-4'-ben- zopyranylidene)methyl]xanthylium perchlorate
68.	2-phenyl-4-{(2'-3'',4''-dimethoxystyryl-3'-phenyl-6'-meth- yl-4'-benzopyranylidene)benzyl]benzopyrylium
<b>69</b> .	perchlorate 2,3-diphenyl-4-{(2'-3'',4''-dimethoxystyryl-3'-phenyl-6'- methyl-4'-benzopyranylidene)benzyl}-6-methylben-
70.	zopyrylium perchlorate 2,3-diphenyl-4-{(2'-3'',4''-dimethoxystyryl-3'-phenyl-6'- methyl-4'-benzopyranylidene)methyl}
71.	-6-methylbenzopyrylium perchlorate  2-p-methoxystyryl-4-{(2'-3'',4''-dimethoxystyryl-3'-phe-nyl-6'-methyl-4'-benzopyranylidene)methyl}ben-
72.	zopyrylium perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-3'',4''-dimethoxysty-ryl-3'-phenyl-6'-methyl-4'-benzopyranylidene)methyl]-
73.	benzopyrylium perchlorate 9-[(2'-3'',4''-dimethoxystyryl-3'-phenyl-6'-methyl-4'-ben-
<b>74</b> .	zopyranylidene)methyl]xanthylium perchlorate  2-phenyl-4-((2'-β-furyl(α')ethenyl-3'-phenyl-6'-methyl-4'- henzopyranylidene)benzyl]benzopyrylium perchlorate
75.	benzopyranylidene)benzyl]benzopyrylium perchlorate 2,3-diphenyl-4-[(2'-β-furyl (α')ethenyl-3'-phenyl-6'-methyl-4'-benzopyranylidene)-
	benzvll-6-methylbenzonyrylium perchlorate

Table 1-continued

Table 1-continued

Com- pound Number	Name of Compound		Com- pound Number	Name of Compound
76.	2,3-diphenyl-4-{(2'-β-furyl(α')ethenyl-3'-phenyl-6'-meth- yl-4'-benzopyranylidene)methyl]-6-methylbenzopyrylium	. ,	118.	2-[(2'-3'',4''-dimethoxystyryl-3'-phenyl-6'-methyl-4'-ben-zopyranylidene)methyl]-3-phenylbenzopyrylium
7 <b>7</b> .	perchlorate 2-p-methoxystyryl-4-[(2'-β-furyl(α')ethenyl-3'-phenyl-6'- methyl-4'-benzopyranylidene)methyl]benzopyrylium		119.	perchlorate 2-[(2'-β-furyl(α')ethenyl-3'-phenyl-6'-methyl-4'-ben- zopyranylidene)methyl]benzopyrylium perchlorate
78.	perchlorate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-β-furyl(α')ethenyl-	10	120.	2-[(2'-β-furyl(α')ethenyl-3'-phenyl-6'-methyl-4'-ben- zopyranylidene)methyl]-3-phenylbenzopyrylium
<b>79</b> .	3'-phenyl-6'-methyl-4'-benzopyranylidene)methyl -ben- zopyrylium perchlorate 9-[(2'-β-furyl(α')ethenyl-3'-phenyl-6'-methyl-4'-ben-		121.	perchlorate 2-[(2'-phenyl-4'-benzothiopyranylidene)methyl]ben- zopyrylium perchlorate
80.	zopyranylidene)methyl]xanthylium perchlorate 2-phenyl-4-[(2'-phenyl-4'-benzothiopyranylidene)benzyl]-		122.	2-[(2'-phenyl-4'-benzothiopyranylidene)methyl]-3- phenylbenzopyrylium perchlorate
81.	benzopyrylium perchlorate 2,3-diphenyl-4-{(2'-phenyl-4'-benzothiopyranylidene)- benzyl]-6-methylbenzopyrylium perchlorate	15	123. 124.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-4-p-methox- yphenylbenzothiopyrylium perchlorate
82.	2,3-diphenyl-4-[(2'-phenyl-4'-benzothiopyranylidene)-methyl]-6-methylbenzopyrylium perchlorate		125.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenyl-4- p-methoxyphenylbenzopyrylium perchlorate 2-[(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)-
83.	2-p-methoxystyryl-4-[(2'-phenyl-4'-benzothi- opyranylidene)methyl]benzopyrylium perchlorate		126.	methyl]-4-p-methoxyphenylbenzothiopyrylium perchlorate 2-[(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)-
84.	2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-benzothi- opyranylidene)methyl]benzopyrylium perchlorate	20		methyl]-3-phenyl-4-p-methoxyphenylbenzothiopyrylium perchlorate
85.	2-p-methoxystyryl-3-phenyl-4-[(2'-phenyl-4'-benzothi- opyranylidene)methyl} -6-methylbenzopyrylium		127.	2-[(2'-phenyl-4'-benzothiopyranylidene)methyl]-4-p- methoxyphenylbenzothiopyrylium perchlorate
86.	perchlorate 2-styryl-3-phenyl-4-[(2'-phenyl-4'-benzothi- opyranylidene)methyl]-6-methylbenzopyrylium		128.	2-[(2'-phenyl-4'-benzothiopyranylidene)methyl]-3-phe- nyl-4-p-methoxyphenylbenzothiopyrylium perchlorate
87.	perchlorate 9-[(2'-phenyl-4'-benzothiopyranylidene)methyl]xan- thylium perchlorate	25	Table 6	
88.	2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-ben- zopyranylidene)methyl]benzopyrylium fluoborate			lists additional information on the absorption makes in dichloroethane and melting point of the

Table 2 lists additional information on the absorption maximum in dichloroethane and melting point of the

89.	zopyranylidene)methyl]benzopyrylium fluoborate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-ben-				and melting point of the to the invention.	
90.	zopyranylidene)methyl]benzopyrylium chloroferrate 2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-ben-		Table 2			
	zopyranylidene)methyl]benzopyrylium chlorozincate	30		- I aon		
91.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-ben-		Compound		Absorption Maximum	
0.2	zopyrylium perchlorate		Number	Melting Point	in dichloroethane $(m\mu)$	
92.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenylben- zopyrylium perchlorate		1	135~139	415 and 710	
93.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenylben-		2	130~139	413 and 710 430 and 720	
, , ,	zopyrylium fluoborate		3	182~187	410 and 630	
94.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenylben-	35	4	164~170	635	
	zopyrylium chloroferrate		5	163~172	490 and 575	
95.	2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenylben-		6	>300	575 and 660	
0.4	zopyrylium nitrate		7	162~169	500 and 610	
96.	2-[(2'-styryl-4'-benzopyranylidene)methyl]benzopyrylium		8	180~187 157~160	490 and 670	
97.	perchlorate 2-[(2'-styryl-4'-benzopyranylidene)methyl]-3-phenylben-		10	103~105	550 and 670 610	
71.	zopytylium perchlorate	40	11	120~126	595	
98.	2-[(4'-benzopyranylidene)methyl]benzopyrylium	40	12	176~180	430 and 700	
	perchlorate		13	122~126	420 and 730	
<b>99</b> .	2-[(4'-benzopyranylidene)methyl]-3-phenylbenzopyrylium		14	163~170	420 and 650	
	perchlorate		15	160~164	500 and 600	
100.	2-[(2'-p-methoxystyryl-4'-benzopyranylidene)methyl]-		16	166~169	495 and 710	
101.	benzopyrylium perchlorate  2.1/2' p. mathorusturul 4' banzonuranulidana (mathul) 3	15	17 18	135~140 159~162	580 555	
101.	2-[(2'-p-methoxystyryl-4'-benzopyranylidene)methyl]-3- phenylbenzopyrylium perchlorate	45	19	179~181	420 and 730	
102.	2-[(4'-benzothiopyranylidene)methyl]benzopyrylium		20	140~142	415 and 730	
	perchlorate		21	165~172	410 and 700	
103.	2-[(4'-benzothiopyranylidene)methyl]-3-phenylben-		22	174~178	500 and 600	
	zopyrylium perchlorate		23	176~179	485	
104.	2-[(2'-3'',4''-dimethoxystyryl-4'-benzopyranylidene)-	= 0	24	170~175	505	
105.	methyl]benzopyrylium perchlorate 2-{(2'-3'',4''-dimethoxystyryl-4'-benzopyranylidene)-	50	25 26	>300 >300	630 560	
105.	methyl]-3-phenylbenzopyrylium perchlorate		27	191~197	560	
10 <del>6</del> .	2-[(2'-β-furyl(α')ethenyl-4'-benzopyranylidene)methyl]-		28	201~203	500 and 590	
	benzopyrylium perchlorate		29	200~204	660 and 710	
107.	2-[(2'-β-furyl(α')ethenyl-4'-benzopyranylidene)methyl]-		30	185~189	410 and 650	
	3-phenylbenzopyrylium perchlorate		31	178~183	430 and 690	
108.	2-[(2'-α-phenylstyryl-4'-benzopyranylidene)methyl]-ben-	55	32 33	181~188	420 and 700	
109.	zopyrylium perchlorate 2-[(2'-α-phenylstyryl-4'-benzopyranylidene)methyl]-3-		34	117~123 185~189	550 and 650 590	
107.	phenylbenzopyrylium perchlorate		35	159~164	495 and 600	
110.	2-{(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)-		36	185~188	610, 650 and 700	
	methyl]benzopyrylium perchlorate		37	160~165	415 and 650	
111.	2-[(2'-α-phenyl-p-methoxystyryl-4'-benzopyranylidene)-		38	204~206	425 and 700	
	methyl]-3-phenylbenzopyrylium perchlorate	<b>6</b> 0	39	166~169	415 and 730	
112.	$2-\{(2'-\alpha-\text{phenyl-}\beta-\text{furyl}(\alpha')\text{ethenyl-}4'-\text{ben-}\alpha-\text{phenyl-}\beta-\text{phenyl-}\beta-\text{phenyl-}\alpha-phenyl$		40 41	>300 173~180	660 555	
	zopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate		42	175~180	540 and 600	
113.	2-[(2'-p-methoxystyryl-3',6'-diphenyl-4'-ben-		43	167~173	660 and 710	
	zopyranylidene)methyl]-3-phenylbenzopyrylium		44	161~164	580 and 720	
	perchlorate		45	145~150	415 and 720	
114.	2-[(2'-3'',4''-dimethoxystyryl-3',6'-diphenyl-4'-ben-	65	46	188~190	425 and 720	
	zopyranylidene)methyl]-3-phenylbenzopyrylium		47	168~175	670	
1.1.5	perchlorate		48 49	171~176 179~186	490 and 580	
115.	2-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl-4'-ben-		50	179~180	600 and 720 610 and 660	
116.	zopyranylidene)methyl]benzopyrylium perchlorate 2-[(2'-p-methoxystyryl-3'-phenyl-6'-methyl-4'-ben-		51	151~155	480 and 740	
410.	zopyranylidene)methyl] 3-phenylbenzopyrylium		52	171~176	495 and 580	
	perchlorate		53	$173 \sim 177$	590 and 700	
117.	2-[(2'-3",4",-dimethoxystyryl-3'-phenyl-6'-methyl-4'-		54	140~147	550 and 750	
	benzopyranylidene)methyl]benzopyrylium perchlorate		55	203~207	420 and 680	

56 138~ 142 555 and 6 57 170~175 570 58 154~157 585 and 6 59 168~174 570	80
57 170~175 570 58 154~157 585 and 69	
59 168~1/4 5/0	90
60 206~209 600	
61 >300 650	
62 139~146 550	
63 202~204 425 and 76	
64 173~177 530 and 69	90
65 190~194 590 66 190~193 500 and 69	00
67 192~195 620	
68 112~118 570 and 7	60
69 190~192 495	Δ0
70 154~159 650 and 79 71 177~182 500 and 7	_
71 177~182 500 Zild 7	
73 195~199 495 and 6	40
74 189~195 550	
75 184~187 415 and 7	
76 192~196 640 and 79 77 >300 550	UU
77 >300 550 78 219~222 550	
79 226~230 630	
80 127~134 410 and 7	45
81 190~192 425 and 7	30
82 156~159 665	.00
83 164~169 600 and 6 84 175~ 178 600 and 7	
85 170~177 550 and 7	
86 157~166 650 and 6	95
87 169~172 635	
88 137~140 500 and 6	_
89 167~172 500 and 6 90 160~163 500 and 6	
91 >300 and 0	,,,,
92 128~134 575 and 6	575
93 133~136 575 and 6	
94 152~158 575 and 6	575
95 133~138 575 96 190~195 575	
97 156~158 620 and 6	<del>9</del> 0
98 225~229 565	
99 183~187 525 and 5	60
100 208~212 570	.00
101 170~176 630 and 6 102 225~228 610	90
102 223~228 010 103 163~168 610 and 6	<b>9</b> 0
104 178~184 510	
105 172~175 580 and 6	
106 167~171 565 and 6	
107 190~194 560 and 6	
108 211~214 370 and 6	_
110 198~201 570 and 6	
111 158~163 580 and 6	
112 > 300 600 and 6 113 185~188 570 and 6	
113 185~188 570 and 6 114 199~204 600	74·V
115 211~215 565 and 6	500
116 177~181 570 and 6	510
117 205~207 570	
118 190~194 590 119 237~241 560	
$119$ $237\sim241$ $560$ $120$ $>300$ $590$	
121 207~210 565 and 6	505
122 155~158 615 and 6	575
123 143~145 615	
124 126~131 619	. <b>5</b> 7
125 144~148 559 and 6 126 140~142 589 and 6	
127 149~153 656	. <del>-</del>
128 141~145 660	

The following description will explain a practical method for making benzopyranylidene-methylben-zopyrylium salts or benzothiopyranylidene-methylben-zopyrylium salts with reference to exemplary compounds. The details of the preparation of other compounds will be apparent to the 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-phenyl-4-[(2'-phenyl-4'-benzopyranylidene)-benzyl]benzopyrylium perchlorate (compund number

5.5 Grams of 2-phenyl-4-methoxybenzopyrylium onitrobenzene sulfonate, which is obtained from flavone and methyl o-nitrobenzenesulfonate, and 5 grams of 2-phenyl-4-benzylbenzopyrylium perchlorate are dissolved in 150 milliliters of acetic anhydride to a solution. The solution is then refluxed for 15 minutes and poured into 900 milliliters of 10 weight percent perchloric acid. The solution is filtered to obtain a precipitate. The precipitate is dried and dissolved again in dichloroethan to a solution. For purification the solution is poured into ether. Precipitated crystals are filtered off, washed with ether and dried to obtain 4 grams (theoretical yield 53%) of green crystals having a melting point of 135° to 139° C.

(b) 2-( $\alpha$ -phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate (compound number 7)

5.5 grams of 2-( $\alpha$ -phenyl-p-methoxystyryl)-4-methylbenzopyrylium perchlorate and 5.5 grams of 2-phenyl-4-methoxybenzopyrylium o-nitrobenzene sulfonate are dissolved in 150 milliliters of acetic anhydride to a solution. The solution is then refluxed for 15 minutes and poured into 900 milliliters of 10 weight percent perchloric acid. The solution is filtered to obtain a precipitate. The precipitate is reprecipitated with dichloroethane ether. Precipitated crystals are filtered off, washed with ether and dried to obtain 5.5 grams (theoretical yield 69%) of blue crystals having a melting point of 162° to 169°C. In the procedure above mentioned the solution ios poured into an ether solution of BF<sub>3</sub>.O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> instead of 10 weight percent Berchloric acid. In this case 2-( $\alpha$ -phenyl-p-methoxystyf $\frac{1}{2}$ )-4-[(2'-phenyl-4'-benzopyranylidene)methyl]benzopyrylium fluoroborate (compound number 88) is obtained. In the procedure when the solution is polified into a 19 weight Bercent zinc chloride aqueous 80lu-

2-(α-phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'benzopyranylidene)-methyl]benzopyrylium zincate (compound number 90) is obtained.

(c) 2-p-methoxystyryl-3-phenyl-4-[(2'-styryl-4'-ben-20pyranylidene)methyl]-6-methylbenzopyrylium per- 5 chlorate (compound number 18)

$$CH = CH - O$$
 $CH = CH - O$ 
 $CH_3$ 
 $CH = CH - O$ 
 $CH_3$ 

$$\left(\begin{array}{c} CH_{3} \\ CH_{3} \end{array}\right)^{-1} CH = CH - \left(\begin{array}{c} CH_{3} \\ CH_{3} \end{array}\right)^{-1} CH_{3}$$

2-styryl-4-methoxybenzopyrylium o-nitrobenzeneulfon (melting point, 155° to 157° C) is obtained by a eaction of 2-styrylchromone and methyl o-nitroben- 30 enesulfonate in dry benzene at 50° C for 24 hours. ccording to the same reaction as shown in procedure 1), 2-styryl-4-methoxybenzopyrylium o-nitrobenzenealfonate reacts with 2-p-methoxystyryl-3-phenyl-4,6imethylbenzopyrylium perchlorate to obtain 2-p- 35 iethoxystyryl-3-phenyl-4-[(2'-styryl-4'-benopyranylidene)methyl]-6-methylbenzopyrylium perhlorate crystals which have a color of reddish violet in ichloroethane and have a melting point of 159° to 62° C. The product is obtained in 73% yield.

2-(α-phenyl-p-methoxystyryl)-4-[(4'-ben-(d) pyranylidene)-methyl]benzopyrylium perchlorate compound number 22)

4-methoxybenzopyrylium o-nitrobenzenesulfonate acts with 2-( $\alpha$ -phenyl-p-methoxystyryl)-4-methyl]-enzopyrylium perchlorate to 2-( $\alpha$ -phenyl-p-methoxstyryl)-4-[(4'-benzopyranylidene)methyl]-benpyrylium perchlorate in the same procedure as the ocedure (a). The crystals have a color of violet in chloroethane and a melting point of 174° to 178°C. he product is obtained in 95% yield.

2-p-methoxystyryl-4-[(2'-3",4"-dimethoxystyryl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate (compound number 42)

CH = CH 
$$\bigcirc$$
 OCH<sub>3</sub>

CH = CH  $\bigcirc$  OCH<sub>3</sub>

CH  $\bigcirc$  OCH<sub>3</sub>

2-(3',4'-Dimethoxystyryl)-4-methoxybenzopyrylium o-nitrobenzenesulfonate (melting point 211° to 213°C) is obtained from a reaction of 2-(3',4'-dimethoxystyryl)chromone and methyl o-nitrobenzene sulfonate. 6.5 Grams of 2-(3',4'-dimethoxystyryl)-4-methoxybenzopyrylium o-nitrobenzenesulfonate and 4,5 grams of 2-p-methoxystyryl-4-methylbenzopyrylium perchlorate are dissolved in 150 milliliters of acetic anhydride to a solution. The solution is heated at 100°C for 100 minutes. After cooling the solution is poured into 900 milliliters of 10 weight percent perchloric acid. Precipitates are filtered off and dried. For purification, reprecipitation is made using dichlorethane and ether. 3.2 Grams of product is obtained in 41% yield. The product has a color of drak violet in dichloroethane and a melting point of 175° to 181°C.

(f) 2-(α-phenyl-p-methoxystyryl)-4-(2'-p-methoxystyryl-3'-phenyl-6'-methyl-4'-benzopyranylidene)me-45 thyl]-benzopyrylium perchlorate (compound number

$$CH = CH - OCH_3$$

$$CH_3 - OCH_3$$

$$CH_3 - OCH_3$$

$$CH_3 - OCH_3$$

$$CH_4 - OCH_3$$

$$CH_5 - OCH_3$$

$$CH_5 - OCH_3$$

2-p-Methoxystyryl-3-phenyl-4-methoxy-6-methylbenzopyrylium o-nitrobenzenesulfonate (melting point 141° to 144°C) is obtained from 2-p-methoxystyryl-3phenyl-6-methylchromone and methyl o-nitrobenzene-sulfonate. 2-p-methoxystyryl-3-phenyl-4-methoxy-6-methylbenzopyrylium o-nitrobenzenesulfonate reacts with 2-(α-phenyl-p-methoxystyryl)-4-methylbenzopyrylium perchlorate in the same procedure as the procedure (e). The product has a color of violet in dichloroethane and a melting point of 190° to 193° C.

(g) 2-p-methoxystyryl-3-phenyl-4-[(2'-phenyl-4'-benzothiopyranylidene)methyl]-6-methyl]benzopyrylium perchlorate (compound number 85)

2-phenyl-4-methoxybenzothiopyrylium o-nitrobenzenesulfonate is obtained from thioflavone and methyl o-nitrobenzenesulfonate. As the same procedure as procedure (e), the product is obtained in 62% yield. 35 The product has a color of reddish violet in dichloroethane and a melting point of 170° to 177° C.

(h) 2-[(2'-phenyl-4'-benzopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate (compound number 92)

5.5 grams of 2-phenyl-4-methoxybenzopyrylium onitrobenzenesulfonate, which is obtained from flavone and methyl o-nitrobenzenesulfonate, and 4 grams of 2-methyl-3-phenylbenzopyrylium perchlorate are dissolved in 150 milliliters of acetic anhydride to a solution. The solution is heated at 100° C for 15 minutes. After cooling the solution is poured into 900 milliliters of 10 weight percent perchloric acid. Precipitated product is filtered off and dried. For purification, reprecipitation is made using dichloroethane and ether. The product has a color of blue in dichloroethane and

a melting point of 128° to 134° C. The product yields 3 grams (theoretical yield 46%). Compound number 93 (fluoborate), compound number 94 (chloroferrate) or compound number 95 (nitrate) is obtained using either solution of borontrifluoride etherate, aqueous solution of ferric chloride or diluted nitric acid respectively instead of 10 weight percent perchloric acid.

(i) 2[(2'- 4 -phenyl-p-methoxystyryl-4'-ben-10 zopyranylidene)methyl]-3-phenylbenzopyrylium perchlorate (compound number 11)

2-(α-Phenyl-p-methoxystyryl)-4-methoxyben-zopyrylium o-nitrobenzenesulfonate, which is obtained from 2-(α-phenyl-p-methoxystyryl)chromone and methyl o-nitrobenzenesulfonate, reacts with 2-methyl-3-phenylbenzopyrylium perchlorate in the same procedure as procedure (h). The reaction product yields in 43%. The product has a color of violet in dichloroethane and a melting point of 158° to 163°C.

It has been discovered according to the invention the compounds listed in Table 1 are sensitizing agents which can improve the photoconductivity and the spectrum characteristics of photoconductive polymeric compounds such as poly-N-vinylcarbazole, brominated poly-N-vinylcarbazoles, polyacenaphthylene, etc. These polymers, except brominated poly-N-vinylcarbazoles, 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 are added 18.44 grams of Nbromosuccinimide and 0.173 grams 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. 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 dichloroethane, methylene chloride, chloroform, or a combination thereof, and is

dded to the solution of the photoconductive polymer lescribed above. The preferable amount of the sensi-izer added is from 0.01 to 3.0 weight parts in connection with 100 weight parts of the photoconductive polymer. Advantageously, the amount thereof is from 0.1 to .0 weight parts in connection with 100 weight parts of he photoconductive polymer.

For the preparation of the photoconductive insulatng layer, a said solution of the photoconductive poly- 10 her and the sensitizer in a suitable solvent is applied to he electroconductive support in per se usual manner, or example, by spraying, by means of bladed coating, y means of whirler coating, etc., and then dried so as o produce a homogeneous photoconductive insulating 15 ayer on the electroconductive support. Operable solents are benzene, toluene, chlorobenzene, dioxane, nethylene chloride, dichloroethane and combinations hereof. Said solution may be incorporated with suitble plasticizers and/or organic colloids for improving  $|_{20}$ he flexibility and strength of the photoconductive polmer. Operable plasticizers are as follows: chlorinated liphenyl, dimethyl phthalate, diethyl phthalate and ctyl phthalate. Operable organic colloids are as folows: natural and synthetic resins, e.g. phenol resin, 25 henol resin modified with resin, polyvinyl acetal, polyinyl butyral, polyvinyl cinnamate, polycarbonate esin. Operable materials for electroconductive suports may be made of any materials which satisfy the equirement of the electrophotographic art, e.g. metal 30 late or glass plate having NESA coating, plate or foil nade of electrically conductive resin or coated with vaporated thin metal layer. If paper is to be used as a upport for the photoconductive layer, pretreatment of he paper against penetration of the coating solution in 35 dvisable. The transparent support can produce a ransparent electrophotographic plate, foil or film. ifter an electrostatic charge has been applied, i.e. after ne layer has been charged positively or negatively by neans of a corona discharge, the layer becomes light 40 ensitive.

The reproduction of images by the electrophotoraphic method is carried out as follows: when the hotoconductive layer has been charged by means of a orona discharge apparatus, the support with the sensized layer is exposed to light under a master and is then usted over in a per se known manner with a resin owder colored with carbon black. The image that now ecomes visible can easily be wiped off. It can also be xed by heating at about 120°C. From positive masters, ositive images characterized by good contrast the roducted.

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

## EXAMPLE 1

I Gram of polyacenaphthylene and 0.6 gram of, as a lasticiser, chlorinated diphenyl (commercially availble as "Kanechlor"), are dissolved in 8 milliliters of hlorobenzene. To the solution are added 0.5 milliliters of dichloroethane containing 0.006 gram of a sensitizer orresponding to compound number listed in Table 1. The solution is applied to an aluminum plate by means of whirler coating and is dried to form a layer of  $7\mu$  in hickness. After said aluminum plate provided with the ayer is charged negatively by means of corona disharge with a charging device maintained at approximately 6000 volts in the dark, it is placed under a positive master and is exposed to a 100W tungsten lamp at n illumination of 50 luxes, and the said plate is powered 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 2, there are shown the optimum amounts of exposure in lux-second units.

Table 2

•	Table 2				
*	Compound Number	Optimum Exposure (lux.sec)			
	none	200000			
	5	320			
	7	300			
5	9	75			
	15	180			
	16	110			
	18	65			
	33	135			
	35	480			
	41	105			
0	42	320			
	51	380			
	52	140			
	53	290			
	54	140			
	58	130			
	60	175			
5	65	140			
	71	180			
	92	70			
	97	150			
	103	001			
	105	120			
	109	130			
0	110	180			
	111	70			
	112	170			
	113	120			
	116	115			

#### **EXAMPLE 2**

I Gram of poly-N-vinylcarbazole, chlorinated diphenyl (commercially available as "Kanechlor") and 0.006 gram of a sensitizer, coresponding to compound number listed in Table 1, in 10 milliliters of dichloroethane to a solution. The solution is applied to an aluminum plate by means of blade coating and is dried to form a layer of  $10\mu$  in thickness. An electrophotographic image in the same way as that described in Example 1. In Table 3, there are shown the optimum amounts of exposure in lux-second units to produced exactly the original images.

Table 3

Compound Number	Optimum Exposure (lux.sec)
none	20000
l	50
2	220
3	60
4	70
5	22
6	44
7	26
8	62
9	44
10	48
11	160
12	220
13	90
14	75
15	28
16	36
17	115
18	22
23	180
26	110
27	44
28	36
29	40
30	60
32	120
33	36
34	50

Table 3-continued

Compound Number	Optimum Exposure (lux.sec)	•
35	30	_
36 37	46 90	3
37 41	52	
42	44	
43	48	•
45	75	
47 40	58 34	10
48 49	35	10
50	70	
51	30	
53	26	
54 54	28	
56 57	28 20	15
58	24	
59	36	
60	44	
61	44	
62	100	
64 65	54 44	20
66	22	20
67	74	
70	56	
71	20	
72	22	
76	60	25
78	38	25
80 82	46 50	
83	24	
84	19	
85	17	
86	54	
87	42 25	30
88 89	25 28	
90	30	
9ĩ	140	
92	18	
93	20	
34	23 40	35
95 96	66	
29	24	
98	230	
99	460	
100	50	
101	36 * 15	40
102 103	115 36	
103	68	
105	19	
106	120	
107	58	
108	76	45
109	46 36	- 🕶
110	36 20	
111 112	42	
113	48	
114	54	
115	54	50
116		J.
	30	
122	28	55
114 115 116 117 118 119 120 121 122	54 52 64 50 135 90 30	
zole.	EXAMPLE 3	60
omo-substituted pr	ed poly-N-vinylcarbazole (mono oduct), 0.5 gram of polycarbon	-

thickness. On this support, electrophotographic images are produced in the same way as that described in Example 1. Table 4 shows the optimum amounts of sposure in lux-second units to reproduce exactly the riginal images.

		Table 4	
	Compound Number	Optimum Exposure (lux.sec)	
10	none	80000 75	
	2	280 67	
	4	44	
	5 6	20 26	
15	7 8	18 30	
	9	22 40	
	10 11	120	
	12 13	400 110	
20	14 15	75 25	
	16	28	
	17 18	135 23	
	19 20	410 340	
25	21 22	180 40	
	23	130 60	
	24 25	300	
	26 27	100 52	
30	28 29	52 48	
	30 31	110 320	
	32	270 27	
	33 34	30	
35	35 37	26 52	
	38 39	440 110	
	40	125 22	
	41 42	28	
40	43 44	32 75	
	45 4 <del>6</del>	105 170	
	47 48	42 32	
	49	35 50	
45	50 51	48	
	52 53	20 19	
	54 55	42 230	
	56 57	26 22	
50	58	24 23	
	59 60	26	
	61 62	36 130	
	63 64	190 44	
55	65 66	26 20	
	67	46	
	68 69	75 115	
	70 71	42 18	
60	72 73	20 48	
	74 75	110 115	
	75 76	70	

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ate 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 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 by means of a blade coating and dried to form a layer of  $14\mu$  in

Table 4-continued

Table 4-continued						
Compound Number	Optimum Exposure (lux.sec)	<del>-</del>				
88	20					
89	20					
90	25					
91	100					
92	15					
93	17					
94	16					
95	40					
96	52					
97	26					
98	180					
99	140					
100	46					
101	36					
102	58					
103	20					
104	34					
105						
	21					
106	80					
107	44					
108	40					
109	23					
110	26					
111	17					
112	26					
113	28					
114	40					
115	44					
116	28					
117	44					
118	36					
119	105					
120	52					
121	26					
122	21					
123	15 .					
124	25					
125	17					
126	14	•				
127	11					
128	13					

It is clear from Table 4 and FIGS. 1 to 9 that the ovel sensitizers improve the photoconductivity and 1e spectrum characteristics of brominated poly-N-inylcarbazole.

The invention has been described in detail with parcular reference to preferred embodiments thereof, ut it will be understood that variations and modificaons can be effected within the spirit and scope of the ivention as described hereinabove and as defined in ne appended claims.

What we claim is:

1. An electrophotographic material comprising a onductive support layer and photoconductive insulating layer, the latter comprising a combination of a hotoconductive polymeric compound and a sensitized amount of a sensitizer having the following formula:

$$\begin{bmatrix} X & & & \\ R_1 & & \\ R_2 & & \\ &$$

herein

B represents a radical selected from the group consting of

$$\begin{array}{c|c}
R_7 & R_5 \\
R_6 & R_8
\end{array}$$

$$x_0$$
 and  $x_0$ 

R<sub>1</sub> is hydrogen, phenyl or an ethenyl radical selected from the group consisting of styryl, p-methoxystyryl, 3,4-dimethoxy-styryl,  $\alpha$ -phenylstyryl,  $\alpha$ -phenyl-p-methoxystyryl,  $\beta$ -furyl( $\alpha'$ ) ethenyl and  $\alpha$ -phenyl- $\beta$ -furyl( $\alpha'$ ) ethenyl;

R<sub>2</sub> is hydrogen or phenyl;

R<sub>3</sub> is hydrogen, methyl or phenyl;

R<sub>4</sub> is hydrogen or phenyl;

 $R_5$  is hydrogen, phenyl or an ethenyl radical selected from the group consisting of styryl, p-methoxystyryl, 3,4-dimethoxy-styryl,  $\alpha$ -phenyl-p-methoxystyryl,  $\beta$ furyl( $\alpha'$ )ethenyl and  $\alpha$ -phenyl- $\beta$ -furyl( $\alpha'$ )ethenyl;

R<sub>6</sub> is hydrogen or phenyl;

R<sub>7</sub> is hydrogen or phenyl;

 $R_8$  is hydrogen or phenyl;

 $R_9$  is hydrogen or p-methoxyphenyl;

the anion is an anionic function selected from the group consisting of perchlorate, fluoroborate, chloroferrate, chlorozincate and nitrate; and

5 X is oxygen or a sulfur atom;

said photoconductive polymeric compound comprising at least one compound selected from the group consisting of poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole and polyacenaphthylene.

- 2. An electrophotographic material according to claim 1, wherein said sensitizer comprises at least one compound selected from the group consisting of 2-( $\alpha$ phenyl-p-methoxystyryl)-4-[(2'-phenyl-4'-benzopyranylidene)methyl]benzopyrylium perchlorate, 55 2-p-methoxystyryl-4-[(2'-3",4"-dimethoxystyryl-3'phenyl-6'-methyl-4'-benzopyranylidene)methyl]benperchlorate, 2-[(2'-phenyl-4'-benzopyrylium zopyranylidene) methyl]-3-phenyl benzopyrylium fluo-2-[(2'-phenyl-4'-benzopyranylidene)me-60 thyl]-4-p-methoxyphenyl benzothiopyrylium perchlorate, and 2-[(2'-phenyl-4'-benzothiopyryanylidene)methyl]-4-p-methoxyphenyl benzothiopyrylium perchlorate.
- 3. An electrophotographic material according to claim 1, wherein said combination comprises 100 weight parts of photoconductive polymeric compound and 0.01 to 3.0 weight parts of sensitizer.