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3,577,235

ELECTROPHOTOGRAPHIC COMPOSITION AND ELEMENT

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U.S. Cl. 96-1.6

10 Claims

ABSTRACT OF THE DISCLOSURE

4-aminobenzo[b]pyrylium and 4-aminobenzo[b]thia-
pyrylium salts are sensitizers for organo-metallic photo-
conductors. Photoconductive compositions sensitized with
these compounds have increased electrophotographic
speed and are sensitive in the ultraviolet region of the
spectrum.

This is a continuation-in-part of U.S. application Ser.
No. 754,499, filed Aug. 21, 1968.

This invention relates to the novel use of a class of
organic compounds as sensitizers in electrophotographic
elements.

The process of xerography, as disclosed by Carlson in
U.S. Pat. No. 2,297,691, employs an electrophotographic
element comprising a support material bearing a coating
of a normally insulating material whose electrical re-
sistance varies with the amount of incident actinic radia-
tion it receives during an imagewise exposure. The ele-
ment, commonly termed a photoconductive element, is
first given a uniform surface charge after a suitable period
of dark adaptation. The element is then exposed to a
pattern of actinic radiation which has the effect of differ-
entially reducing the potential of the surface charge in
accordance with the relative energy contained in various
parts of the radiation pattern. The differential surface
charge or electrostatic latent image remaining on the
electrophotographic element is then made visible by
contacting the surface with a suitable electroscopic mark-
ing material. Such marking material or toner, whether
contained in an insulating liquid or on a dry carrier,
can be deposited on the exposed surface in accordance
with either the charge pattern or in the absence of charge
pattern as desired. The deposited marking material may
then be either permanently fixed to the surface of the
sensitive element by known means such as heat, pressure,
solvent vapor and the like or transferred to a second
element to which it may similarly be fixed. Likewise,
the electrostatic latent image can be transferred to a sec-
ond element and developed there.

Various photoconductive insulating materials have been
employed in the manufacture of electrophotographic ele-
ments. For example, vapors of selenium and vapors of
selenium alloys deposited on a suitable support and par-
ticles of photoconductive zinc oxide held in a resinous,
film-forming binder have found wide application in pres-
ent-day document copying applications.

Since the introduction of electrophotography, a great
many organic compounds have been found to possess
some degree of photoconductivity. Many organic com-
pounds have revealed a useful level of photoconduction
and have been incorporated into photoconductive com-
positions. In addition, many organo-metallic photocon-
ductive compounds have been found to be very useful.
Optically clear organo-metallic photoconductor-contain-
ing elements having desirable electrophotographic prop-
erties can be especially useful in electrophotography. Such

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electrophotographic elements may be exposed through a
transparent base, if desired, thereby providing unusual
flexibility in equipment design. Such compositions when
coated as a film or layer on a suitable support also yield
an element which is reusable; that is, it can be used
to form subsequent images after residual toner from prior
images has been removed by transfer and/or cleaning.

Although some of the various photoconductor mate-
rials referred to above are inherently light sensitive, their
degree of sensitivity is usually low and not always in
a desired wavelength portion of the spectrum so that
it is common practice to add materials to increase the
speed and to shift the spectral sensitivity.

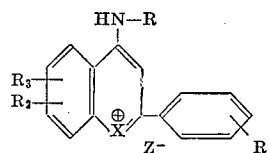
Increasing the speed and shifting the sensitivity of
such systems has several advantages in that it reduces
exposure time, allows projection printing through various
optical systems etc. By increasing the speed through
the use of sensitizers, photoconductors which would
otherwise have been unsatisfactory are useful in processes
where higher speeds are required. However, a major dis-
advantage of many of the prior sensitized photoconductor
systems has been the highly colored nature of such
systems.

It is, therefore, an object of this invention to provide
a novel class of sensitizers for use in combination with
organo-metallic photoconductors.

Another object of this invention is to provide novel
sensitized photoconductive elements.

A further object of this invention is to provide novel
photoconductive compositions which are colorless and
are sensitive to ultraviolet radiation.

These and other objects are accomplished by the use
of 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]thia-
pyrylium salts as sensitizers in organo-metallic photo-
conductor-containing systems. Typical sensitizers of the
present invention include those having the following struc-
tural formula:



wherein:

X is a sulfur atom or an oxygen atom;
Z is an anionic function including such acid anions
as perchlorate, fluoroborate, sulfonate, periodate, p-tolu-
enesulfonate etc.;

R is an alkyl radical typically having 1 to 10 carbon
atoms, such as methyl, ethyl, isopropyl, n-butyl, pentyl,
octyl, decyl etc. including cycloalkyl such as cyclopentyl,
cyclohexyl etc., as well as such substituted alkyl radicals
as aralkyl radicals typically having 1 to 4 carbon atoms
in the alkyl moiety such as benzyl, phenylethyl, phenyl-
propyl and phenylbutyl; an aryl radical such as phenyl
and naphthyl radicals; and the like;

R1 is a hydrogen atom, a lower alkyl radical typical-
ly having 1 to 4 carbon atoms such as methyl, ethyl,
isopropyl, butyl etc. and a lower alkoxy radical typical-
ly having 1 to 4 carbon atoms in the alkyl moiety such
as methoxy, ethoxy, propoxy, butoxy etc.; and

R2 and R3 when taken separately each represents a
hydrogen atom and when taken together are attached
to adjacent carbon atoms and represent the atoms neces-
sary to form a fused aromatic ring such as a benzo
ring and including substituted fused aromatic rings.

Suitable sensitizers would include the following representative compounds:

TABLE A

Name	
Number:	
1.....	4-benzylamino-2-phenylbenzo[b]pyrylium perchlorate.
2.....	4-anilino-2-(4-methoxyphenyl)naphtho[1,2-b]pyrylium perchlorate.
3.....	1-(N-butylamino)-3-phenylnaphtho[2,1-b]pyrylium perchlorate.
4.....	4-(N-butylamino)-2-(4-methoxyphenyl)naphtho[1,2-b]pyrylium perchlorate.
5.....	1-anilino-3-phenylnaphtho[2,1-b]pyrylium perchlorate.
6.....	4-(N-butylamino)-2-phenylbenzo[b]thiapyrylium perchlorate.
7.....	4-anilino thiapyrylium perchlorate.
8.....	4-cyclohexylamino-2-phenylbenzo[b]thiapyrylium perchlorate.
9.....	4-(N-octylamino)-2-phenylbenzo[b]thiapyrylium perchlorate.
10.....	4-phenylamino-2-phenylbenzo[b]thiapyrylium perchlorate.
11.....	2-phenyl-4-phenethylaminobenzo[b]thiapyrylium perchlorate.
12.....	4-(N-butylamino)-2-(p-methoxyphenyl)benzo[b]pyrylium fluoroborate.
13.....	4-(N-butylamino)-2-(p-methoxyphenyl)benzo[b]pyrylium perchlorate.
14.....	4-benzylamino-2-phenylbenzo[b]thiapyrylium perchlorate.
15.....	4-(N-n-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium fluoroborate.

Electrophotographic elements of the invention can be prepared with a variety of organo-metallic photoconductive compounds and the sensitizing compounds of this invention in the usual manner, i.e., by blending a dispersion or solution of the photoconductive compound together with an electrically insulating, film-forming resin binder when necessary or desirable and coating or forming a self-supporting layer with the photoconductive composition. Generally, a suitable amount of the sensitizing compound is mixed with the photoconductive coating composition so that after thorough mixing the sensitizing compound is uniformly distributed throughout the desired layer of the coated element. The amount of sensitizer that can be added to a photoconductor-containing layer to give effective increases in speed can vary widely. The optimum concentration in any given case will vary with the specific photoconductor and sensitizing compound used. In general, substantial speed gains can be obtained where an appropriate sensitizer is added in a concentration range from about 0.0001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount from about 0.005 to about 5.0 percent by weight of the total coating composition.

The sensitizers of this invention are effective for enhancing the electrophotosensitivity of a wide variety of organometallic photoconductors. The photoconductors used are these organo-metallic compounds which exhibit an electrophotosensitivity to light and are capable of forming transparent elements. A class of organo-metallic photoconductors which are particularly well suited for use with the present sensitizers includes organo-metallic compounds which are the organic derivatives of Group IIIa, IVa or Va metals such as those having at least one aminoaryl group attached to the metal atom and as described in copending Johnson U.S. patent application Ser. No. 755,711, filed Aug. 27, 1968 and Goldman and Johnson, U.S. patent application Ser. No. 650,664, filed July 3, 1967.

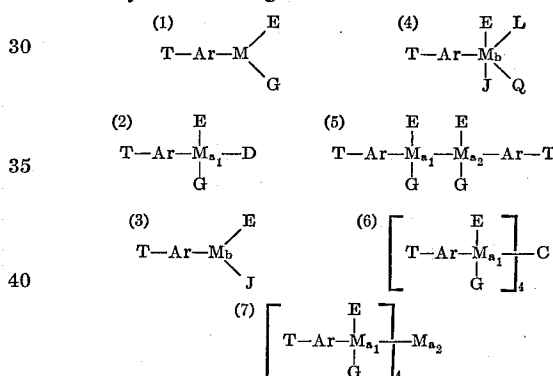
The metallic substituents of these organo-metallic photoconductors are Group IIIa, Group IVa or Group Va metals in accordance with the Periodic Table of the Elements (Handbook of Chemistry and Physics, 38th edition, pp. 394-95) and include boron, aluminum, gallium, indium, and thallium from Group IIIa, silicon, germanium, tin and lead from Group IVa and phosphorus, arsenic, antimony and bismuth from Group Va. The organo-metallic photoconductors useful in this invention can be substituted on the metal nucleus with a wide variety of substituents but at least one of the substituents must be an aminoaryl radical. The amino radical can be positioned anywhere on the aromatic nucleus, but best results are obtained if the aryl moiety is a phenyl radical having the amino group in the 4 or para position. Typical substituents attached to the metal nucleus include the following:

- (a) a halogen, sulfur or oxygen atom,
- (b) an alkyl radical, including substituted alkyl radicals,

- (c) an aryl radical including substituted aryl radicals such as aminoaryl, alkylaryl and haloaryl,

- (d) an oxygen-containing radical such as an alkoxy or aryloxy radical,
- (e) an amino radical including substituted amino radicals such as mono- and diarylamino and mono- and dialkyl-amino radicals,
- (f) a heterocyclic radical, and
- (g) a Group IIIa, IVa or Va organo metallic radical.

Illustrative photoconductors of this invention are represented by the following structures:



wherein:

- E, G, L and Q can be:
- (a) a hydrogen atom;
- (b) an aryl radical including substituted and unsubstituted aryl radicals such as a phenyl radical, a naphthyl radical, a dialkylaminophenyl radical, etc.;
- (c) an alkyl radical having 1 to 8 carbon atoms;
- (d) an alkoxy radical having 1 to 8 carbon atoms;
- (e) an aryloxy radical such as a phenoxy radical;
- (f) an amino radical having the formula



- wherein R₁ and R₂ can be hydrogen atoms or alkyl radicals having 1 to 8 carbon atoms; or
- (g) a heterocyclic radical having 5 to 6 atoms in the hetero nucleus including at least one nitrogen atom such as a triazolyl, a pyridyl radical, etc.;

T is an amino radical including substituted amino radicals such as an alkylamino radical having 1 to 8 carbon atoms or an arylamino radical such as a phenylamino or naphthylamino radical;

Ar is an aromatic radical such as phenylene or naphthylene;

M is a Group IIIa metal;

M_{a1} and M_{a2} are the same or different Group IVa metals;

M_b is a Group Va metal;

D can be any of the substituents set forth above for

E, G, L and Q and in addition can be a Group IVa organo-metallic radical, or when taken with E, an oxygen atom or a sulfur atom;

J can be any of the substituents set forth above for E, G, L and Q, and when taken with E, an oxygen atom or a sulfur atom.

Some typical organo-metallic photoconductors of this invention include the compounds listed below:

TABLE I

Number:	Name
16.....	Triphenyl-p-diethylaminophenylsilane.
17.....	Methyl-diphenyl-p-diethylaminophenylsilane.
18.....	Triphenyl-p-diethylaminophenylgermane.
19.....	Triphenyl-p-dimethylaminophenylstannane.
20.....	Triphenyl-p-diethylaminophenylstannane.
21.....	Diphenyl-bis-(p-diethylaminophenyl)stannane.
22.....	Triphenyl-p-diethylaminophenylplumbane.
23.....	Tetra-p-diethylaminophenylplumbane.
24.....	Tetra-p-diethylaminophenylgermane.
25.....	Phenyl-bis-(p-diethylaminophenyl)phosphine.
26.....	Bis-(p-diethylaminophenyl)phosphine oxide.
27.....	Tris-p-dimethylaminophenylarsine.
28.....	Tris-p-diethylaminophenylarsine.
29.....	2-methyl-4-dimethylaminophenylarsine oxide.
30.....	Tris-p-diethylaminophenylbismuthine.
31.....	Methyl-bis-(p-diethylaminophenyl)arsine.
32.....	Methyl-bis-(p-diethylaminophenyl)phosphine.
33.....	Diphenyl-p-diethylaminophenylsilane.
34.....	p-Diethylaminophenylarsine.
35.....	4,4',4''-tris(diethylamino)tetraphenylstannane.
36.....	Tetrakis-[diphenyl-(p-diethylaminophenyl)plumbyl]methane.
37.....	Tetrakis-[diphenyl-(p-diethylaminophenyl)stannyl]stannane.
38.....	Bis-[phenyl-(p-diethylaminophenyl)]dibismuthine.
39.....	Tris-(p-diethylaminophenyl)phosphine sulfide.
40.....	Bis-(p-diethylaminophenyl)thioxostannane.
41.....	Bis[2-mesityl-4-(N-piperidino)phenyl]borane.
42.....	Bis[2-mesityl-4-(N,N-dimethylamino)phenyl]borane.
43.....	Tri-p-diethylaminophenylborane.
44.....	Tri-p-diphenylaminophenylborane.
45.....	Tri-p-methylaminophenylgallium.
46.....	Methyl-phenyl-p-diethylaminophenylborane.
47.....	2-naphthyl-p-dimethylaminophenylborane.
48.....	p-Dipropylaminophenylborane.
49.....	Di-p-diethylaminophenylborane.
50.....	Ethoxy-p-dimethylaminophenyl aluminum hydride.
51.....	Diphenoxy-p-dibutylaminophenyl aluminum.
52.....	Tri-(2,6-dimethoxy-4-diethylaminophenyl)indium.
53.....	2-chloro-4-dimethylaminophenyl gallium hydride.
54.....	Tri-(2,6-diphenoxy-4-diethylaminophenyl)thallium.
55.....	Tri-(2,6-dimethoxy-4-dimethylaminophenyl)thallium.
56.....	Diphenylamino-p-diethylaminophenylborane.
57.....	Dimesityl-4-dimethylaminonaphthylborane.
58.....	Dimesityl-4-dimethylaminophenylborane.
59.....	Dimesityl-(3,5-dimethyl-4-methoxyphenyl)borane
60.....	Dimesityl-4-diphenylaminophenylborane.
61.....	1,2-bis(p-diethylaminophenyl)diborane.
62.....	1-phenyl-2-methyldiborane.

The organo-metallic photoconductors useful in the present invention can generally be prepared by known methods. For example, the aminoaryl lead and tin compounds can be prepared in accordance with J. Am. Chem. Soc., 54, 3726-9 (1932) or J. Org. Chem., 15, 994 (1950). The aminoaryl germanium compounds are made by the method set forth in Chem. Abstracts, 60, p. 395d. A method for making the aminoaryl bismuthines has been described by Gilman and Yablunky (J. Am. Chem. Soc., 63, 207-211 [1941]). Aminoaryl derivatives of arsenic are prepared in accordance with J. Indian Chem. Soc., 16, 515-518 (1939). Phosphorus and antimony compounds containing aminoaryl moieties may be prepared by methods described in Chem. Abstracts, 28, 3392³ and Chem. Abstracts, 40, 46896, respectively.

Preferred binders for use in preparing the present photoconductive layers comprise polymers having fairly high dielectric strength which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resin; styrene-alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride-acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly(isobutyl methacrylate), etc.; polystyrene, nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylene alkaryloxyalkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamide; polycarbonates; polythio-

carbonates; poly(ethyleneglycol-co-bishydroxyphenyl propane terephthalate); nuclear substituted polyvinyl haloarlates; etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Pats. 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of the invention are sold under such trade names

as Vitel PE-101, Cymac, Piccopale 100, Saran F-220 and Lexan 105. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

Solvents of choice for preparing coating compositions of the present invention can include a number of solvents such as benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc.

In preparing the coating composition useful results are obtained where the photoconductor substance is present in an amount equal to at least about 1 weight percent of the coating composition. The upper limit in the amount of photoconductor substance present can be widely varied in accordance with usual practice. In those cases where a binder is employed, it is normally required that the photoconductor substance be present in an amount from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductor substance in the coating composition is from about 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally, a coating in the range of about 0.001 inch to about 0.01 inch before drying is useful for the practice of this invention. The preferred range of coating thickness is found to be in the range from about 0.002 inch to about 0.006 inch before drying although useful results can be obtained outside of this range.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foils such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass and galvanized plates; vapor deposited metal layers such as silver, nickel, aluminum and the like coated on paper of conventional photographic film bases such as cellulose acetate, polystyrene, etc. Such conducting materials as nickel can be coated by vacuum deposition on transparent film supports in sufficiently thin layers to allow electrophotographic elements prepared therewith to be exposed from either side of such elements. An especially useful conducting support can be prepared by coating a support material such as poly(ethylene terephthalate) with a conducting layer containing a semiconductor dispersed in a resin. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxy-ester lactone of maleic anhydride and a vinyl acetate polymer. Such kinds of conducting layers and methods for their optimum preparation and use are disclosed in U.S. 3,007,901 and 3,267,807.

The elements of the present invention can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the aforementioned xerographic process. As explained previously, in a process of this type the electrophotographic element is given a blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained on the layer by virtue of the substantial insulating property of the layer, i.e., the low conductivity of the layer in the dark. The electrostatic charge formed on the surface of the photoconductive layer is then selectively dissipated from the surface of the layer by exposure to light through an image-bearing transparency by a conventional exposure operation such as, for example, by contact-printing technique, or by lens projection of an image, etc., to form an electrostatic latent image in the photoconducting layer. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that light causes the charge to be conducted away in proportion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then developed, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust or a pigment in a resinous carrier or a liquid developer can be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature in such patents, for example, as U.S. 2,297,691 and in Australian Pat. 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has a low-melting resin as one of its components, it is possible to treat the developed photoconductive material with heat and cause the powder to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the image formed on the photoconductive layer can be made to a second support which would then become the final print. Techniques of the type indicated are well known in the art and have been described in a number of U.S. and foreign patents such as U.S. Pats. 2,297,691 and 2,551,582 and in "RCA Review," vol. 15 (1954), pages 469-484.

An increasing use of electrophotographic elements has occurred in the field of recording data displayed on a cathode-ray tube. Advantages gained through such use include attractively high photographic speed, desirable

spectral response, and short time of access to a visible recorded image.

It is frequently desirable to employ the image-bearing electrophotographic element having a transparent film base as a master from which further prints can be generated. Such elements can be used as masters in many types of reproduction processes. Typical of these processes are the xerographic process, thermographic process, direct electrostatic process, stabilization process, gelatin transfer process, diffusion transfer process, etc. A particularly advantageous process by which such a print can be made is the diazo process. In this process, a diazonium salt-containing element is exposed through a transparent electrophotographic original bearing a developed or toned image to activating radiation from an ultraviolet source. The exposure causes decomposition of the salt in those areas which are struck by activating radiation. Subsequently, the exposed diazo element is passed through an atmosphere of a suitable alkaline material, such as ammonia vapor. In the presence of the alkaline material and a dye-forming coupler, which can be either incorporated in the diazonium-containing layer or introduced during the development step, the diazonium salt which is not decomposed by exposure is converted to an azo dye. A positive reproduction of the original is formed.

A difficulty commonly encountered in the production of copies from sensitized photoconductor-containing coated elements is that the photoconductive element possesses a relatively high optical opacity resulting from coloration imparted by the sensitized photoconductor-containing composition. As a result the element does not transmit sufficient radiation in that portion of the electromagnetic spectrum to which the copy element is sensitive. Therefore, reprints are very difficult to obtain. Also, if the image-bearing elements are to be used for direct reading, the image portions of the elements are often almost indiscernible due to the lack of contrast. One solution proposed for this problem has been to bleach the highly colored photoconductive element. However, with the present class of sensitizers, a colorless photoconductive layer results which eliminates the need for an extra bleaching step.

The photoconductive compositions of the present invention are particularly sensitive in the ultraviolet region of the spectrum. Because of this short wavelength sensitivity, the standard test procedures for compositions sensitive in the visible region of the spectrum are not particularly meaningful when testing the present composition. One of the major reasons for not using standard test procedures is that they usually involve exposure to a 3000° K. tungsten light source. A light source of this nature is relatively deficient in ultraviolet radiation and thus such a test procedure would not adequately measure the unique characteristic of the present compositions. Accordingly, the speed of the photoconductive compositions according to the present invention are best shown when measured in terms of the time required to photodecay, upon exposure to an ultraviolet source, from an initial surface potential, V_0 , to some lower predetermined surface potential V . This photodecay test is described further in Example 1. Of course, some increase in speed can be seen even when measurement is made using a tungsten source and standard test procedures as described further in Example 4.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A control coating is prepared from the following ingredients:

- 1.5 g. polycarbonate resin formed from the reaction between phosgene and a dihydroxydiarylalkane or from the ester exchange reaction between diphenylcarbonate and 2,2-bis-(4-hydroxyphenyl)propane (binder)
- 0.5 g. 4,4',4''-tris(diethylamino)tetraphenyl tin (photoconductor)
- 11.7 ml. methylene chloride (solvent)

The above homogeneous photoconductive composition is coated at a wet thickness of 0.004 inch onto a poly(ethylene terephthalate) film support carrying a conductive layer of the sodium salt of a polymeric lactone as described in U.S. Pat. No. 3,260,706. During the coating step, the coating block temperature is maintained at 90° F. The resultant electrophotographic element is called Element 1 (control). The above procedure is then repeated with the addition of 0.01 g. 4-(N-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium perchlorate as a sensitizer in the photoconductive compositions. The resultant element is colorless and is designated Element 2. Next, the two elements are measured for speed in a photodecay test as follows. The elements are electrostatically charged positively or negatively under a corona source until the surface potential, as measured by an electrometer probe, reaches about 600 volts. The charged elements are then exposed with a 365 m μ line exposure. After exposure, the time required for the surface charge to decay to a value of 100 volts is noted. The relative response of each element is then expressed in terms of the time (in seconds) required for the element to photodecay from 600 to 100 volts. This time measurement is referred to as the positive or negative 100 volt photodecay time. The decay times of the elements are recorded in Table I below.

TABLE I

Element number	100 volt photodecay time, seconds	
	Positive	Negative
1-----	>>60	>>60
2-----	1.9	4.1

These elements can then be charged, imagewise exposed and developed with a liquid developer of the type described in U.S. Pat. No. 2,907,674 to form visible images.

EXAMPLE 2

Three electrophotographic elements are prepared by the general procedure of Example 1 using 1.5 g. of poly(vinyl-m-bromobenzoate-co-vinylacetate) as the binder, 0.5 g. of tetra-p-diethylaminophenylgermane as the photoconductor, 11.7 ml. of solvent and varying amounts of the sensitizer 4-(N-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium perchlorate. Elements 3, 4 and 5 contain 1, 2 and 3 weight percent, respectively. The elements are then charged to +600 volts as in the previous example. The charged elements are then exposed to a xenon light source through a 1.9 neutral density filter in combination with a set of filters simulating the wavelength distribution of the emission spectrum of a P-16 phosphor. A P-16 phosphor is a standard phosphor used in cathode ray tubes. This phosphor fluoresces in the ultraviolet to blue spectral region with an emission peak at 3800 Å. The P-16 phosphor is comprised of calcium magnesium silicate doped with cesium. After exposure, the times required for the surface charge to decay to 100 and to 50 volts are noted. The relative response of each element is then expressed in terms of the time (in seconds) required for the element to photodecay from 600 to 100 volts and to 50 volts. These decay time measurements are shown in Table II below.

TABLE II

Element number	Photodecay time, seconds	
	+100 volts	+50 volts
3-----	48.8	>60
4-----	19.5	32.3
5-----	16.9	25.9

As in Example 1, these elements can be charged, imagewise exposed and developed with a suitable developer to form visible images.

EXAMPLE 3

Four electrophotographic elements are prepared as in the previous examples. The binder used in all the elements is the same as in Example 2. Element 6 contains tetra-p-diethyl-aminophenylplumbane as the photoconductor with no sensitizer. Element 7 contains the same photoconductor as Element 6 with 1% by weight of 4-(N-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium perchlorate as the sensitizer. Element 8 contains 4,4'-bis-(diethylamino)triphenylarsine as the photoconductor with no sensitizer. Element 9 contains the same photoconductor as Element 8 with 1% of the sensitizer of Element 7. The elements are then charged, exposed and measured for their positive and negative 100 volt photodecay times as in Example 1. These measurements are shown in Table III below.

TABLE III

Element number	100 volt photodecay time, seconds	
	Positive	Negative
6 (control)-----	23.0	23.6
7-----	9.8	10.8
8 (control)-----	6.5	10.8
9-----	3.4	3.9

As in the preceding examples, these elements can be charged, imagewise exposed and developed to form visible images.

EXAMPLE 4

Four electrophotographic elements are prepared by the general procedure of Example 1 using 1.5 g. of poly(vinyl-m-bromobenzoate-co-vinylacetate) as the binder in each, 0.5 g. of 4,4'-bis(diethylamino)triphenylarsine as the photoconductor in elements 10 and 11, 0.5 g. of 4,4',4''-tris(diethylamino)tetraphenylstannane as the conductor in elements 12 and 13, varying amounts of 4-(N-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium perchlorate as in the sensitizer in elements 10, 11 and 12 and 2% by weight of 4-cyclohexylamino-2-phenylbenzo[b]thiapyrylium perchlorate as the sensitizer in element 13. The resultant electrophotographic elements are then electrostatically charged under a corona source until the surface potential, as measured by an electrometer probe, reaches about 600 volts. The charged elements are then exposed to a 3000° K. tungsten light source through a stepped density gray scale. The exposure causes reduction of the surface potential of the elements under each step of the gray scale from its initial potential, V₀, to some lower potential, V, whose exact value depends on the actual amount of exposure in meter-candle-seconds received by the area. The results of these measurements are then plotted on a graph of surface potential V vs. log exposure for each step. The actual positive or negative speed of the photoconductive composition used can then be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily selected value. In this example, the actual positive or negative speed is the numerical expression of 10⁴ divided by the exposure in meter-candle-seconds required to reduce the 600 volt charged surface potential to a value of 500 volts (100 volt shoulder speed) or to a value of 100 volts (100 volt toe speed). The speeds of the elements are recorded in Table IV below.

TABLE IV

Element Number	Amount of sensitizer weight percent	+100 volt	
		shoulder speed	Toe speed
10 (control)-----		53	0
11-----	1	105	5.6
12-----	2	120	11
13-----	2	90	5

These elements can then be charged, exposed and developed with dry developers of the type described in U.S. Reissue Patent No. 25,136 to form visible images.

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EXAMPLE 5

Five electrophotographic elements are prepared by the general procedure of Example 1 using 1.5 g. of the binder of Example 1, 0.5 g. of 4,4',4''-tris(diethylamino)tetraphenylstannane as the photoconductor and 0.1% by weight of the sensitizer shown in Table V below. The elements are charged, exposed and their positive and negative 100 volt shoulder speeds are measured as in Example 4. The results of these measurements are shown in Table V below.

TABLE V

Element Number	Sensitizer	100 volt shoulder speed	
		Positive	Negative
14 (control)		13	11
15	4-(N-n-butylamino)-2-(4-methoxyphenyl)naphtho[1,2-b]pyrylium perchlorate.	150	82
16	4-benzylamino-2-phenylbenzo[b]pyrylium perchlorate.	41	38
17	4-(N-n-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium fluoroborate.	95	66
18	4-benzylamino-2-phenylbenzo[b]thiapyrylium perchlorate.	63	55

These elements can then be charged, exposed and developed with dry developers of the type described in U.S. Reissue Patent No. 25,136 to form visible images.

EXAMPLE 6

Two electrophotographic elements are prepared by the general procedure of Example 1 using 1.5 g. of Vitel 101 as the binder and 0.375 g. of bis[2-mesityl-4-(N-piperidino)phenyl]borane as the photoconductor. The control element (No. 19) contains no sensitizer; whereas the other element (No. 20) contains 0.0375 g. of 4-(N-n-butylamino)-2-(4-methoxyphenyl)benzo[b]pyrylium perchlorate. Vitel 101 is a polymer obtained from Goodyear Tire & Rubber Co. and is a polyester of terephthalic acid and 2,2-bis[4-(β -hydroxyethoxy)phenyl]propane in which the substituted propane is replaced in a 50:50 molar ratio with ethylene glycol. These two elements are charged, exposed and measured for positive and negative 100 v. shoulder speeds as in Example 4 only using an unfiltered xenon source. The results of these measurements are shown in Table VI below.

TABLE VI

Element Number	100 volt shoulder speed	
	Positive	Negative
19 (control)	250	63
20	630	250

The elements can be charged, imagewise exposed and developed as in the preceding examples to form a visible image.

EXAMPLE 7

Example 6 is repeated using bis[2-mesityl-4-(N,N-dimethylamino)phenyl]borane as the photoconductor, with no sensitizer in the control element (No. 21) and the sensitizer of Example 6 in the sensitized element (No. 22). The resulting positive and negative 100 v. shoulder speeds are shown in Table VII below.

TABLE VII

Element Number	100 volt shoulder speed	
	Positive	Negative
21 (control)	200	50
22	800	450

The elements thus formed can be charged, exposed and developed as in the preceding examples.

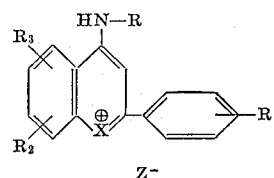
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The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photoconductive composition comprising an organo-metallic photoconductor, an electrically insulating, film-forming resin binder and a sensitizing amount of a member selected from the group consisting of 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]thiapyrylium salts, said photoconductor being selected from the group consisting of a Group IIIa organo-metallic compound having at least one aminoaryl radical attached to a Group IIIa metal, a Group IVa organo-metallic compound having at least one aminoaryl radical attached to a Group IVa metal and a Group Va organo-metallic compound having at least one aminoaryl radical attached to a Group Va metal.

2. A photoconductive composition as in claim 1 wherein the 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]thiapyrylium salts have the formula:



wherein:

X is selected from the group consisting of a sulfur atom and an oxygen atom;

Z is an anion;

R is selected from the group consisting of an alkyl radical and an aryl radical;

R₁ is selected from the group consisting of a hydrogen atom, a lower alkyl radical and a lower alkoxy radical; and

R₂ and R₃ when taken separately each represent a hydrogen atom and when taken together are attached to adjacent carbon atoms and represent the atoms necessary to form a fused aromatic ring.

3. A photoconductive composition as in claim 1 wherein the 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]thiapyrylium salts are selected from the group consisting of:

4-benzylamino-2-phenylbenzo[b]pyrylium perchlorate,

4-anilino-2-(4-methoxyphenyl)naphtho[1,2-b]pyrylium perchlorate,

1-(N-butylamino)-3-phenylnaphtho[2,1-b]pyrylium perchlorate,

4-(N-butylamino)-2-(4-methoxyphenyl)naphtho[1,2-b]pyrylium perchlorate,

1-anilino-3-phenylnaphtho[2,1-b]pyrylium perchlorate,

4-(N-butylamino)-2-phenylbenzo[b]thiapyrylium perchlorate,

4-anilino flavylium perchlorate,

4-cyclohexylamino-2-phenylbenzo[b]thiapyrylium perchlorate,

4-(N-octylamino)-2-phenylbenzo[b]thiapyrylium perchlorate,

4-phenylamino-2-phenylbenzo[b]thiapyrylium perchlorate,

2-phenyl-4-phenethylaminobenzo[b]thiapyrylium perchlorate,

4-(N-butylamino)-2-(p-methoxyphenyl)benzo[b]pyrylium fluoroborate,

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- 4 - (N - butylamino) - 2 - (p - methoxyphenyl)benzo-
[b]pyrylium perchlorate,
4 - (N - n - butylamino) - 2 - (4 - methoxyphenyl)
benzo[b]pyrylium fluoroborate, and
4 - benzylamino - 2 - phenylbenzo[b]thiapyrylium per-
chlorate.

4. A photoconductive composition as in claim 1 where-
in the organo-metallic photoconductor is selected from
the group consisting of:

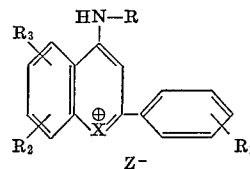
triphenyl-p-diethylaminophenylsilane,
methyl-diphenyl-p-diethylaminophenylsilane,
triphenyl-p-diethylaminophenylgermane,
triphenyl-p-dimethylaminophenylstannane,
triphenyl-p-diethylaminophenylstannane,
diphenyl-bis-(p-diethylaminophenyl)stannane,
triphenyl-p-diethylaminophenylplumbane,
tetra-p-diethylaminophenylplumbane,
tetra-p-diethylaminophenylgermane,
phenyl-bis-(p-diethylaminophenyl)phosphine,
bis-(p-diethylaminophenyl)phosphine oxide,
tris-p-dimethylaminophenylarsine,
tris-p-diethylaminophenylarsine,
2-methyl-4-dimethylaminophenylarsine oxide,
tris-p-diethylaminophenylbismuthine,
methyl-bis-(p-diethylaminophenyl)arsine,
methyl-bis-(p-diethylaminophenyl)phosphine,
diphenyl-p-diethylaminophenylsilane,
p-diethylaminophenylarsine,
4,4',4''-tris(diethylamino)tetraphenylstannane,
tetrakis - [diphenyl - (p - diethylaminophenyl)plumbyl]
methane,
terakis - [diphenyl - (p - diethylaminophenyl)stannyl]
stannane,
bis-[phenyl-(p-diethylaminophenyl)]dibismuthine,
tris-(p-diethylaminophenyl)phosphine sulfide,
bis-(p-diethylaminophenyl)thioxostannane,
bis[2-mesityl-4-(N-piperidino)phenyl]borane,
bis[2 - mesityl - 4 - (N,N - dimethylamino)phenyl]
borane,
tri-p-diethylaminophenylborane,
tri-p-diphenylaminophenylborane,
tri-p-methylaminophenylgallium,
methyl-phenyl-p-diethylaminophenylborane,
2-naphthyl-p-dimethylaminophenylborane,
p-dipropylaminophenylborane,
di-p-diethylaminophenylborane,
ethoxy-p-dimethylaminophenyl aluminum hydride,
diphenoxy-p-dibutylaminophenyl aluminum,
tri-(2,6-dimethyl-4-diethylaminophenyl)indium,
2-chloro-4-dimethylaminophenyl gallium hydride,
tri-(2,6-diphenoxy-4-diethylaminophenyl)thallium,
tri-(2,6-dimethoxy-4-dimethylaminophenyl)thallium,
diphenylamino-p-diethylaminophenylborane,
dimesityl-4-dimethylaminonaphthylborane,
dimesityl-4-dimethylaminophenylborane,
dimesityl-(3,5-dimethyl-4-methoxyphenyl)borane,
dimesityl-4-diphenylaminophenylborane,
1,2-bis(p-diethylaminophenyl)diborane, and
1-phenyl-2-methyldiborane.

5. An electrophotographic element comprising a sup-
port having coated thereon a layer of a photoconductive
composition containing an organo-metallic photoconduc-
tor and a sensitizing amount of a member selected from
the group consisting of 4-aminobenzo[b]pyrylium and 4-
aminobenzo[b]thiapyrylium salts, said photoconductor
being selected from the group consisting of a Group IIIa
organo-metallic compound having at least one amino-
aryl radical attached to a Group IIIa metal, a Group IVa
organo-metallic compound having at least one aminoaryl
radical attached to a Group IVa metal and a Group Va
organo-metallic compound having at least one aminoaryl
radical attached to a Group Va metal.

6. An electrophotographic element as in claim 5 where-

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in the 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]
thiapyrylium salts have the formula:



wherein:

X is selected from the group consisting of a sulfur
atom and an oxygen atom;

Z is an anion;

R is selected from the group consisting of an alkyl
radical and an aryl radical;

R₁ is selected from the group consisting of a hydrogen
atom, a lower alkyl radical and a lower alkoxy radi-
cal; and

R₂ and R₃ when taken separately each represents a hy-
drogen atom, and when taken together are attached to
adjacent carbon atoms and represent the atoms
necessary to form a fused aromatic ring.

7. An electrophotographic element as in claim 5 where-
in the 4-aminobenzo[b]pyrylium and 4-aminobenzo[b]
thiapyrylium salts are selected from the group consisting
of:

- 4-benzylamino-2-phenylbenzo[b]pyrylium perchlorate,
4 - anilino - 2 - (4 - methoxyphenyl)naphtho[1,2-b]
pyrylium perchlorate,
1 - (N - butylamino) - 3 - phenylnaphtho[2,1-b]
pyrylium perchlorate,
4 - (N - butylamino) - 2 - (4 - methoxyphenyl)naphtho-
[1,2-b]pyrylium perchlorate,
1-anilino-3-phenylnaphtho[1,2-b]pyrylium perchlorate,
4 - (N - butylamino) - 2 - phenylbenzo[b]thiapyrylium
perchlorate,
4-anilino flavylium perchlorate,
4 - cyclohexylamino - 2 - phenylbenzo[b]thiapyrylium
perchlorate,
4 - (N - octylamino) - 2 - phenylbenzo[b]thiapyrylium
perchlorate,
4 - phenylamino - 2 - phenylbenzo[b]thiapyrylium
perchlorate,
2 - phenyl - 4 - phenethylaminobenzo[b]thiapyrylium
perchlorate,
4 - (N - butylamino) - 2 - (p - methoxyphenyl)benzo-
[b]pyrylium fluoroborate,
4 - (N - butylamino) - 2 - (p - methoxyphenyl)benzo-
[b]pyrylium perchlorate,
4 - (N - n - butylamino) - 2 - (4 - methoxyphenyl)
benzo[b]pyrylium fluoroborate, and
4 - benzylamino - 2 - phenylbenzo[b]thiapyrylium
perchlorate.

8. An electrophotographic element as in claim 5 where-
in the support is electrically conducting.

9. An electrophotographic element as in claim 5 where-
in the organo-metallic photoconductor is selected from
the group consisting of:

- triphenyl-p-diethylaminophenylsilane,
methyl-diphenyl-p-diethylaminophenylsilane,
triphenyl-p-diethylaminophenylgermane,
triphenyl-p-dimethylaminophenylstannane,
triphenyl-p-diethylaminophenylstannane,
diphenyl-bis-(p-diethylaminophenyl)stannane,
triphenyl-p-diethylaminophenylplumbane,
tetra-p-diethylaminophenylplumbane,
tetra-p-diethylaminophenylgermane,
phenyl-bis-(p-diethylaminophenyl)phosphine,
bis(p-diethylaminophenyl)phosphine oxide,
tris-p-dimethylaminophenylarsine,
tris-p-diethylaminophenylarsine,
2-methyl-4-dimethylaminophenylarsine oxide,
tris-p-diethylaminophenylbismuthine,
methyl-bis-(p-diethylaminophenyl)arsine,

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methyl-bis-(p-diethylaminophenyl) phosphine,
 diphenyl-p-diethylaminophenylsilane,
 p-diethylaminophenylarsine,
 4,4',4''-tris(diethylamino)tetraphenylstannane,
 tetrakis - [diphenyl - (p - diethylaminophenyl)plumbyl] 5
 methane,
 tetrakis - [diphenyl - (p - diethylaminophenyl)stannyl]
 stannane,
 bis-[phenyl-(p-diethylaminophenyl)] dibismuthine,
 tris-(p-diethylaminophenyl) phosphine sulfide,
 bis-(p-diethylaminophenyl) thioxostannane,
 bis[2-mesityl-4-(N-piperidino)phenyl] borane,
 bis[2-mesityl-4-(N,N-dimethylamino)phenyl] borane,
 tri-p-diethylaminophenylborane,
 tri-p-diphenylaminophenylborane,
 tri-p-methylaminophenylgallium,
 methyl-phenyl-p-diethylaminophenylborane,
 2-naphthyl-p-dimethylaminophenylborane,
 p-dipropylaminophenylborane,
 di-p-diethylaminophenylborane,
 ethoxy-p-dimethylaminophenyl aluminum hydride,
 diphenoxy-p-dibutylaminophenyl aluminum,
 tri-(2,6-dimethyl-4-diethylaminophenyl) indium,
 2-chloro-4-dimethylaminophenyl gallium hydride,
 tri-(2,6-diphenoxy-4-diethylaminophenyl) thallium,
 tri-(2,6-dimethoxy-4-dimethylaminophenyl) thallium,
 diphenylamino-p-diethylaminophenylborane,
 dimesityl-4-dimethylaminonaphthylborane,

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dimesityl-4-dimethylaminophenylborane,
 dimesityl-(3,5-dimethyl-4-methoxyphenyl) borane,
 dimesityl-4-diphenylaminophenylborane,
 1,2-bis(p-diethylaminophenyl) diborane, and
 1-phenyl-2-methyldiborane.

10. An electrophotographic element as described in claim 5 wherein the organo-metallic photoconductor is selected from the group consisting of:

4,4',4''-tris(diethylamino) tetraphenylstannane,
 tetra-p-diethylaminophenylgermane,
 4,4'-bis(diethylamino) triphenylarsine,
 bis[2-mesityl-4-(N-piperidino)phenyl] borane, and
 bis[2-mesityl-4-(N,N-dimethylamino)phenyl] borane.

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CHARLES E. VAN HORN, Primary Examiner

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96—1.5; 252—501; 260—239, 327, 345.2, 429, 429.7,
 437, 440, 446, 447, 448, 448.2