Photoconductive Composition and Elements Containing a Styryl Amino Group Containing Photoconductor

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Assignee: Eastman Kodak Company, Rochester, N.Y.

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Application No.: 443,657

Related U.S. Application Data

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Int. Cl. G03g 5/06

Field of Search 96/1.5, 1.6; 260/240 D, 260/571, 576

References Cited
UNITED STATES PATENTS
3,189,447 6/1965 Neugebauer et al. 96/1.5
3,246,983 4/1966 Sus et al. 96/1.5
3,265,497 8/1966 Kosche 96/1.5
3,615,396 10/1971 Granza et al. 96/1.6
3,615,414 10/1971 Light 96/1.6
3,615,415 10/1971 Granza 96/1.6
3,653,887 4/1972 Merrill 96/1.5 X
3,825,534 7/1974 Weber et al. 96/1.5 X

Primary Examiner—Roland E. Martin, Jr.  
Attorney, Agent, or Firm—R. P. Hilst

ABSTRACT

A novel photoconductive composition and electrophotographic elements containing the same are prepared using as a photoconductor a compound having a central carbocyclic or sulfur heterocyclic divalent aromatic ring joined to two amino-substituted styryl radicals through the vinylene groups of the styryl radicals.

13 Claims, No Drawings
PHOTOCONDUCTIVE COMPOSITION AND ELEMENTS CONTAINING A STYRYL AMINO GROUP CONTAINING PHOTOCONDUCTOR

This application is a continuation-in-part of Ser. No. 357,441, filed May 4, 1973, now abandoned. Reference is made also to Contois and Rossi, U.S. patent application Ser. No. 443,655, filed concurrently here- with, and entitled "Aggregate Photoconductive Compositions and Elements Containing Same".

FIELD OF THE INVENTION

This invention relates to electrophotography and in particular to photoconductive compositions and ele-

DESCRIPTION OF THE PRIOR ART

The process of xerography, as disclosed by Carlson in U.S. Pat. No. 2,297,691, employs an electropho-
graphic element comprising a support material bearing a coating of an insulating material whose electrical re-
sistance varies with the amount of incident electromagnetic radiation it receives during an imagewise ex-
sposure. The element, commonly termed a photoconduc-
tive element, is first given a uniform surface charge, generally in the dark after a suitable period of dark ad-
aptation. It is then exposed to a pattern of actinic radia-
tion which has the effect of differentially reducing the potential of this surface charge in accordance with the relative energy contained in various parts of the radia-
tion pattern. The differential surface charge or electro-
static latent image remaining on the electrophoto-
graphic element is then made visible by contacting the surface with a suitable electroscoptic marking 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 discharge pattern as desired. Depo-
sited marking material can then be either perma-
nently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor or the like, or transferred to a second element to which it can similarly be fixed. Likewise, the electrostatic charge pattern can be transferred to a second element and developed there.

Various photoconductive insulating materials have been employed in the manufacture of electrophoto-
graphic elements. For example, vapors of selenium and vapors of selenium alloys deposited on a suitable sup-
port and particles of photoconductive zinc oxide held in a resinous, film-forming binder have found wide ap-
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Since the introduction of electrophotography, a great many organic compounds have also been screened for their photoconductive properties. As a result, a very large number of organic compounds have been known to possess some degree of photoconductivity. Many or-

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Since the introduction of electrophotography, a great many organic compounds have also been screened for their photoconductive properties. As a result, a very large number of organic compounds have been known to possess some degree of photoconductivity. Many or-

ties can be especially useful in electrophotography. Such electrophotographic element can be exposed through a transparent base if desired, thereby providing 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. Thus far, the selection of various compounds for incorporation into photoconductive compositions to form electrophotographic layers has proceeded on a compound-by-compound basis. Nothing as yet has been discovered from the large number of different photoconductive substances tested which permits ef-
fектив prediction, and therefore selection of the particu-
lar compounds exhibiting the desired electrophotographic properties.

A high speed "heterogeneous" or "aggregate" multi-
phase photoconductive system was developed by Wil-
liam A. Light which overcomes many of the problems of the prior art. This aggregate photoconductive com-
position (as it is referred to herein) is the subject matter of U.S. Pat. No. 3,615,414 issued Oct. 26, 1971. The addenda disclosed therein are responsible for the exhibition of desirable electrophotographic properties in photoconductive elements prepared therewith. In particular, they have been found to enhance the speed of many organic photoconductors when used there-
with. The degree of such enhancement is, however, variable, depending on the particular organic photo-
conductor so used.

SUMMARY OF THE INVENTION

In accord with the present invention there is provided a novel photoconductive composition comprising as a photoconductor a compound having a central carbocyclic or sulfur heterocyclic divalent aromatic ring joined to two amino-substituted styryl radicals through the vi-

ylene groups of the styryl radicals.

In accord with one embodiment of the invention, we have found that the distyryl-containing aromatic com-

mounds may be used as the photoconductive material of a homogeneous organic photoconductive conduc-
tive composition.

In accord with another embodiment of the present inven-
tion, it has been discovered that one or more of these distyryl-containing aromatic compounds may be em-
ployed as the only organic photoconductor in the continuous polymer phase of a multiphase aggregate photoconductive composition of the type referred to herein above to extend the white light speed and blue sensitivity of the aggregate photoconductive composi-
tion.

In accord with still another embodiment of the inven-
tion, we have found that the distyryl-containing aro-
matic compounds may be incorporated as a photocon-
ductive material in a photoconductive composition which also contains one or more inorganic photocon-
ductors. For example, photoconductive compositions comprising a mixture of the above-described distyryl-
containing aromatic compounds and lead oxide provide elements exhibiting useful xeroradiographic prop-
erties.

Various closely related compounds having a cyano-
substituted vinylene moiety in place of the unsubstit-
tuted vinylene moieties contained in the photoconduc-
tive compounds used in the present invention have
been described in the prior art. Representative of such prior art materials are compounds having the following formula:

![Chemical Structure](image)

wherein Am represents an amino group and Ar represents a divalent aromatic group. See Merrill, U.S. Pat. No. 3,653,887 issued Apr. 4, 1972.

According to the present invention, it has been found that the photoconductors described herein have substantially improved electrical speed over those related photoconductors described in U.S. Pat. No. 3,653,887.

In addition, it has been found that the photoconductors of the present invention enhance the blue sensitivity of aggregate photoconductive compositions in comparison to the use of other known prior art compounds employed in similar aggregate photoconductive compositions, for example the triarylamines shown in U.S. Pat. No. 3,180,730 and certain of the active hydrogen-containing photoconductive materials shown in Brantly et al., U.S. Pat. No. 3,567,450.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred photoconductors of the invention may be characterized by the following formula:

![Chemical Structure](image)

wherein R1, R2, R3, and R4, which can be the same or different, represent alkyl or aryl radicals including substituted alkyl and aryl radicals;

Ar1 and Ar2, which can be the same or different, represent an unsubstituted or a substituted phenyl radical having one or more substituents selected from the group consisting of an alkyl, aryl, alkoxy, arylamino, and halogen substituent; and

Ar3 represents a carbocyclic or sulfur heterocyclic, monocyclic or polycyclic, aromatic ring typically containing 4 to 14 carbon atoms in the ring such as pheny, naphthyl and anthryl aromatic groups as well as substituted aromatic groups having one or more substituents selected from the group of substituents defined above as substituents for Ar1 and Ar2.

Typically, R1, R2, R3, and R4 represent one of the following alkyl or aryl groups:

1. an alkyl group having one to 18 carbon atoms e.g., methyl, ethyl, propyl, butyl, isobutyl, octyl, dodecyl, etc. including a substituted alkyl group having one to 18 carbon atoms such as

   a. alkoxalkyl e.g., ethoxypropyl, methoxybutyl, propoxyethyl, etc.
   b. aryloxalkyl e.g., phenoxyethyl, napthoxymethyl, phenoxyethyl, etc.
   c. aminoalkyl e.g., aminobutyl, aminoethyl, aminopropyl, etc.
   d. hydroxalkyl e.g., hydroxypropyl, hydroxyoctyl, etc.

2. an aryl group e.g., benzyl, phenethyl, etc.

   f. alkyaminooalkyl e.g., methyaminopropl, methylaminooethyl, methyaminooctyl, etc., and also including dialkyaminooalkyl e.g., diethyaminooethyl, dimethyaminooctyl, propyaminooctyl, etc.
   g. arlyaminooalkyl, e.g., phenylaminooalkyl, diphenylaminooalkyl, N-phenyl-N-ethylaminopentyl, N-phenyl-N-ethylaminohexyl, naphthylaminomethyl, etc.
   h. nitroalkyl, e.g., nitrobutyl, nitroethyl, nitropentyl, etc.
   i. cyanoalkyl, e.g., cyanopropyl, cyanoethyl, etc., and
   j. haloalkyl, e.g., chloromethyl, bromopentyl, chlorooctyl, etc.

k. alkyl substituted with an acyl group having the formula

![Chemical Structure](image)

wherein R is hydroxy, hydrogen, aryl, e.g., phenyl, naphthyl, etc., lower alkyl having one to eight carbon atoms e.g., methyl, ethyl, propyl, etc., amino including substituted amino, e.g., diloweralkylamino, lower alkyl having one to eight carbon atoms, e.g., butoxyl, methoxy, etc., arlyoxyl, e.g., phenoxy, naphthoxy, etc.

or

2. an aryl group, e.g., phenyl, naphthyl, anthryl, fluoroaryl, etc., including a substituted aryl group such as

   a. alkyloxarylg, e.g., ethoxyphenyl, methoxophenyl, propoxynaphthyl, etc.
   b. aryloxaryl, e.g., phenoxyphenyl, naphthoxyphenyl, phenoxynaphthyl, etc.
   c. aminoaryl, e.g., aminophenyl, aminonaphthyl, aminanthryl, etc.
   d. hydroxaryl, e.g., hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc.
   e. biphenyl

   f. alkyaminooaryl, e.g., methyaminophenyl, methylaminonaphthyl, etc. and also including dialkyaminooaryl, e.g., diethyaminophenyl, dipropylaminophenyl, etc.
   g. arlyaminooaryl, e.g., phenylaminophenyl, diphenylaminophenyl, N-phenyl-N-ethylaminophenyl, naphthylaminophenyl, etc.
   h. nitroaryl e.g., nitrophenyl, nitronaphthyl, nitroanthryl, etc.
   i. cyanoaryl, e.g., cyanophenyl, cyanonaphthyl, cyananthryl, etc.
   j. haloaryl, e.g., chlorophenyl, bromophenyl, chloroanthryl, etc.

   k. alkaryl, e.g., tolyl, ethylphenyl, propynaphthyl, etc., and

l. aryl substituted with an acyl group having the formula

![Chemical Structure](image)

wherein R is hydroxy, hydrogen, aryl, e.g., phenyl, naphthyl, etc., amino including substituted amino, e.g., diloweralkylamino, lower alkyl having one to eight carbon atoms, e.g., butoxyl, methoxy, etc., arlyoxyl, e.g., phenoxy, naphthoxy, etc., lower alkyl having one to...
eight carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc.
Typically, when either Ar₁ or Ar₂ represent a substituted phenyl radical the substituents on the phenyl radical are alkyl or aryl groups as defined above for R₁, R₂, R₃, R₄ or also any of the following:
1. an alkoxy group having one to 18 carbon atoms, e.g., methoxy, ethoxy, propoxy, butoxy, etc.,
2. an aryloxy group e.g., phenoxy, naphthoxy, etc.; and
3. halogen such as chlorine, bromine, fluorine or iodine.
Typical compounds which belong to the general class of photoconductive compounds described herein include the following materials listed in Table I below:

### TABLE I

<table>
<thead>
<tr>
<th>Compound Description</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) 4-Diphenylamino-4′-[4-diphenylamino) styryl] stilbene having the formula</td>
<td>209-211°</td>
</tr>
<tr>
<td>((C_6H_5)_2N)CH=CH-CH=CH-CH=CH-N(p-C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(II) 4-Di-(p-tolylamino)-4′-[4-(di-p-tolylamino)styryl] stilbene having the formula</td>
<td>216-220°</td>
</tr>
<tr>
<td>((p-CH₃C₆H₄)₂)N)CH=CH-CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(III) 4-Di-(p-tolylamino)-2′,3′,5′,6′-tetramethyl-4′-[4-(di-p-tolylamino)styryl] stilbene having the formula</td>
<td>231-233°</td>
</tr>
<tr>
<td>((p-CH₃C₆H₄)₂)N)CH=CH-CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(IV) 4-Di-(p-tolylamino)-2′- [4-(di-p-tolylamino)styryl] stilbene having the formula</td>
<td>106-108°</td>
</tr>
<tr>
<td>((p-CH₃C₆H₄)₂)N)CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(V) 4-Di-(p-tolylamino)-2′,4′-dimethyl-5′-[4-(di-p-tolylamino) styryl] stilbene having the formula</td>
<td>211-215°</td>
</tr>
<tr>
<td>((p-CH₃C₆H₄)₂)N)CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(VI) 9,10-Bis[4-(di-p-tolylamino)styryl] anthracene having the formula</td>
<td>288-290°</td>
</tr>
<tr>
<td>((p-CH₃C₆H₄)₂N)CH=CH-CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(VII) ((p-CH₃C₆H₄)₂N)CH=CH-CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
<tr>
<td>(VIII) 1,4-Bis[4-N-ethyl-N-p-tolylaminostyryl] benzene having the formula</td>
<td>204-206°</td>
</tr>
<tr>
<td>(CH₃)CH=CH-CH=CH-CH=CH-N(p-CH₃C₆H₄)₂</td>
<td></td>
</tr>
</tbody>
</table>
Compounds which belong to the general class of photoconductive compounds described herein and which are preferred for use in accord with the present invention include those compounds having the structural formula shown above wherein \( R_1, R_2, R_3, \) and \( R_4 \) are aryl groups as defined above, particularly tolyl radicals, and wherein \( A_1, A_2, \) and \( A_3 \) are unsubstituted phenyl radicals or alkyl substituted phenyl radicals having no more than two alkyl substituents, said alkyl substituents containing 1 or 2 carbon atoms.

As set forth hereinabove, in accord with one embodiment of the invention, the photoconductive compounds of the invention can be used in aggregate photoconductive compositions of the present invention. Those distyryl-containing aromatic compounds noted above as especially preferred have been found particularly useful in aggregate photoconductive compositions because of their ability to increase the blue sensitivity of these aggregate compositions and because of their unexpected ability to increase the speed of these aggregate compositions in comparison to the photoconductive materials shown in U.S. Pat. No. 3,653,887 which have a very similar molecular structure.

The aggregate compositions used in this invention comprise an organic sensitizing dye and an electrically insulating, film-forming polymeric material. They may be prepared by several techniques, such as, for example, the so-called “dye first” technique described in Gramza et al., U.S. Pat. No. 3,615,396 issued Oct. 26, 1971. Alternatively, they may be prepared by the so-called “shearing” method described in Gramza, U.S. Pat. No. 3,615,415 issued Oct. 26, 1971. This latter method involves the high speed shearing of the photoconductive composition prior to coating and thus eliminates subsequent solvent treatment, as was disclosed in Light, U.S. Pat. No. 3,615,414 referred to above. By whatever method prepared, the aggregate composition is combined with the distyryl-containing photoconductor of the invention in a suitable solvent to form a photoconductor-containing composition which is coated on a suitable support to form a separately identifiable multiphase composition, the heterogeneous nature of which is generally apparent when viewed under magnification, although some compositions may appear to be substantially optically clear to the naked eye in the absence of magnification. There can, of course, be macroscopic heterogeneity. Suitably, the dye-containing aggregate in the discontinuous phase is predominantly in the size range of from about 0.01 to about 25 microns.

In general, the aggregate compositions formed as described herein are multiphase organic solids containing dye and polymer. The polymer forms an amorphous matrix or continuous phase which contains a discrete discontinuous phase as distinguished from a solution.

The discontinuous phase is the aggregate species which is a co-crystalline complex comprised of dye and polymer.

The term co-crystalline complex as used herein has reference to a crystalline compound which contains dye and polymer molecules co-crystallized in a single crystalline structure to form a regular array of the molecules in a three-dimensional pattern.

Another feature characteristic of the aggregate compositions formed as described herein is that the wavelength of the radiation absorption maximum characteristic of such compositions is substantially shifted from the wavelength of the radiation absorption maximum of a substantially homogeneous dye-polymer solid solution formed of similar constituents. The new absorption maximum characteristic of the aggregates formed by this method is not necessarily an overall maximum for this system as this will depend upon the relative amount of dye in the aggregate. Such an absorption maximum shift in the formation of aggregate systems for the present invention is generally of the magnitude of at least about 10 nm. If mixture of dyes are used, one dye may cause an absorption maximum shift to a long wavelength and another dye cause an absorption maximum shift to a shorter wavelength. In such cases, a formation of the aggregate compositions can more easily be identified by viewing under magnification.

Sensitizing dyes and electrically insulating polymeric materials are used in forming these aggregate compositions. Typically, pyrylium dyes, including pyrylium, bispyrylium, thiapyrylium and selenapyrylium dye salts and also salts of pyrylium compounds containing condensed ring systems such as salts of benzopyrylium and naphthopyrylium dyes are useful in forming such compositions. Dyes from these classes which may be useful are disclosed in Light U.S. Pat. No. 3,615,414.

Particularly useful dyes in forming the feature aggregates are pyrylium dye salts having the formula:

\[
\text{R}_5 \text{R}_6 \text{R}_7 \text{X} \text{Z}^-
\]

wherein:

- \( \text{R}_5 \) and \( \text{R}_6 \) can each be phenyl radicals, including substituted phenyl radicals having at least one substituent chosen from alkyl radicals of from 1 to about 6 carbon atoms and alkoxy radicals having from 1 to about 6 carbon atoms;
- \( \text{R}_7 \) can be an alkylamino-substituted phenyl radical having from 1 to 6 carbon atoms in the alkyl moiety, and including dialkylamino-substituted and haloalkylamino-substituted phenyl radicals;
- \( \text{X} \) can be an oxygen or a sulfur atom; and
- \( \text{Z}^- \) is an anion.

The polymers useful in forming the aggregate compositions include a variety of materials. Particularly useful are electrically insulating, film-forming polymers having an alkyldiene diarylene moiety in a recurring unit such as those linear polymers, including copolymers, containing the following moiety in a recurring unit:
wherein:

R₉ and R₁₀, when taken separately, can each be a hydrogen atom, an alkyl radical having from one to about 10 carbon atoms such as methyl, ethyl, isobutyl, hexyl, heptyl, octyl, nonyl, decyl, and the like including substituted alkyl radicals such as trifluoromethyl, etc., and an aryl radical such as phenyl and naphthyl, including substituted aryl radicals having such substituents as a halogen atom, an alkyl radical of from 1 to about 5 carbon atoms, etc.; and R₉ and R₁₀, when taken together, can represent the carbon atoms necessary to complete a saturated cyclic hydrocarbon radical including cycloalkanes such as cyclo-hexyl and polycycloalkanes such as norbornyl, the total number of carbon atoms in R₉ and R₁₀ being up to about 19; R₈ and R₁₁, can each be hydrogen, an alkyl radical of from 1 to about 5 carbon atoms, etc., or a halogen such as chloro, bromo, iodo, etc.; and R₁₂ is a divalent radical selected from the following:

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymeric Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>poly(4,4'-isopropylidenediphenylene-co-1,4-cyclohexylmethylene carbonate)</td>
</tr>
<tr>
<td>2</td>
<td>poly(ethylenedioxy-3,3'-phenylene thiocarbonate)</td>
</tr>
<tr>
<td>3</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate-co-terephthalate)</td>
</tr>
<tr>
<td>4</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>5</td>
<td>poly(4,4'-isopropylidenediphenylene thiocarbonate)</td>
</tr>
<tr>
<td>6</td>
<td>poly(4,4'-sec-butylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>7</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate-block-oxetane)</td>
</tr>
<tr>
<td>8</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate-block-oxetane)</td>
</tr>
<tr>
<td>9</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate-block-oxetane)</td>
</tr>
<tr>
<td>10</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>11</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>12</td>
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</tr>
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<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>15</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>16</td>
<td>poly(4,4'-isopropylidenediphenylene carbonate)</td>
</tr>
<tr>
<td>17</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
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<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
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<td>33</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>34</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>35</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<td>36</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>37</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>38</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>39</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>40</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>41</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<tr>
<td>42</td>
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<td>43</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<td>46</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>47</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>48</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
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<td>50</td>
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</tr>
<tr>
<td>51</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>52</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>53</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>54</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
<tr>
<td>55</td>
<td>poly[1,1,1-(p-bromophenylethyl)idenebis(1,4-phenylene carbonate)]</td>
</tr>
</tbody>
</table>

Preferred polymers useful for forming aggregate crystals are hydrophobic carbonate polymers containing the following moiety in a recurring unit:

![Chemical structure](image)

wherein:
each R is a phenylene radical including halo substituted phenylene radicals and alkyl substituted phenylene radicals; and R₉, R₁₀, R₁₁, and R₁₂ are as described above. Such compositions are disclosed, for example in U.S. Pat. Nos. 3,028,365 and 3,317,466. Preferably polycarbonates containing an alkylene diarylene moiety in the recurring unit such as those prepared with Bisphenol A and including polymeric products of ester exchange between diphenylcarbonate and 2,2-bis-(4-hydroxyphenyl)-propane are useful in the practice of this invention. Such compositions are disclosed in the following U.S. Patents: U.S. Pat. No. 2,999,750 by Miller et al., issued Sept. 12, 1961; U.S. Pat. No. 3,038,874 by Laakso et al., issued June 12, 1962; U.S. Pat. No. 3,038,879 by Laakso et al., issued June 12, 1962; U.S. Pat. No. 3,038,880 by Laakso et al., issued June 12, 1962; U.S. Pat. No. 3,106,544 by Laakso et al., issued Oct. 8, 1963; U.S. Pat. No. 3,106,545 by Laakso et al., issued Oct. 8, 1963; and U.S. Pat. No. 3,106,546 by Laakso et al., issued Oct. 8, 1963. A wide range of film-forming polycarbonate resins are useful, with completely satisfactory results being obtained when using commercial polymeric materials which are characterized by an inherent viscosity of about 0.5 to about 1.8.

The following polymers are included among the materials useful in the practice of this invention:
Electrophotographic elements of the invention containing the above-described aggregate photoconductive composition can be prepared by blending a dispersion or solution of the photoconductive composition together with a binder, when necessary or desirable, and coating or forming a self-support layer with the materials. Supplemental materials useful for changing the spectral sensitivity or electrophotosensitivity of the element can be added to the composition of the element when it is desirable to produce the characteristic effect of such materials. If desired, other polymers can be incorporated in the vehicle, for example, to alter physical properties such as adhesion of the photoconductive layer to the support and the like. Techniques for the preparation of aggregate photoconductive layers containing such additional vehicles are described in C. L. Stephens, U.S. Pat. No. 3,679,407, issued July 25, 1972, and entitled METHOD OF FORMING HETEROGENEOUS PHOTOCONDUCTIVE COMPOSITIONS AND ELEMENTS. The photoconductive layers of the invention can also be sensitized by the addition of effective amounts of sensitizing compounds to exhibit improved electrophotosensitivity.

The amount of distyryl-containing photoconductor incorporated into the aggregate photoconductive compositions and elements of the invention can be varied over a relatively wide range. However, when used as a photoconductor in an aggregate photoconductive composition the distyryl-containing compound should be present in the continuous phase of the aggregate composition and should be present in an amount in excess of about 15 percent by weight (based on the dry weight of the aggregate photoconductive composition). Small amounts of the distyryl-containing compound (i.e., amounts less than about 15 percent by weight of the total dry weight of the aggregate photoconductive composition) may be advantageously incorporated in an aggregate photoconductive composition (as described in the previously cross-referenced co-pending Contois and Rossi, U.S. patent application Ser. No. 443,655), as an additive in combination with a non-blue light absorbing organic photoconductor to provide enhanced resistance to electrical fatigue, improved temperature stability, and enhanced blue sensitivity. But, in accord with the present invention, larger amounts of the distyryl-containing compound (e.g., amounts in the range of 15 to 35 weight percent or more) are incorporated in the continuous polymer phase of an aggregate photoconductive composition as the sole organic photoconductor contained in said continuous phase, thereby significantly increasing the overall white light electrophotographic speed of the resultant aggregate composition as well as providing enhanced blue sensitivity. At the same time, however, aggregate photoconductive compositions containing very large amounts of the distyryl-containing compound (i.e., amounts on the order of about 25 weight percent or more) do not appear to exhibit as good electrical fatigue resistance (sometimes referred to as charge regeneration) as is provided when smaller amounts of the distyryl-containing compound is incorporated therein as an additive in combination with a non-blue light absorbing organic photoconductor. Accordingly, aggregate photoconductive compositions of the present invention which contain a large amount of the distyryl-containing aromatic compound as a photoconductor are particularly useful, for example, in electrophotographic elements and processes requiring relatively high speed non-reusable photoconductive compositions. In contrast, small amounts of the distyryl-containing aromatic compound are particularly useful as an additive for a reusable aggregate photoconductive composition, which even without the distyryl-containing aromatic compound possesses a white light speed at or near the desired level, to provide improved resistance to electrical fatigue, improved temperature stability, and enhanced blue light sensitivity.

In addition to electrophotographic elements containing the above-described aggregate photoconductive compositions there are other useful embodiments of the present invention. For example, “non-aggregate-containing” electrophotographic elements can be prepared with the photoconductive compounds of the invention in the usual manner, i.e., by blending a dispersion or solution of a photoconductive compound together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the photoconductor-containing materials. Mixtures of the photoconductors described herein can be employed. Likewise, other inorganic and organic photoconductors known in the art can be combined with the present photoconductors. In addition, supplemental materials useful for changing the spectral sensitivity or electrophotosensitivity of the element can be added to the composition of the element when it is desirable to produce the characteristic effect of such materials.

The non-aggregate photoconductive layers of the invention such as homogeneous organic photoconductive compositions, photoconductive compositions comprising an organic compound used in the present invention together with an inorganic compound such as lead oxide, and the like can be sensitized by the addition of effective amounts of sensitizing compounds to exhibit improved electrophotosensitivity. Sensitizing compounds useful with the photoconductive compounds of the present invention can be selected from a wide variety of materials, including such materials as pyrylium dye salts including thiapyrylium dye materials as pyrylium dye salts including thiapyrylium dye salts and selenapyrylium dye salts disclosed in VanAllan et al U.S. Pat. No. 3,250,615; fluorones, such as 7,12-dioxo-13-dibenzo(a,h)fluorene, 5,10-dioxo-4a,11-diazabenzof(b)-fluorene, 3,13-dioxo-7-oxadbenzof(b,g)fluorene, and the like; aromatic nitro compounds of the kinds described in U.S. Pat. No. 2,610,120; anthrones like those disclosed in U.S. Pat.
3,873,312

No. 2,670,284; quinones, U.S. Pat. No. 2,670,286; benzophenones U.S. Pat. No. 2,670,287; thiazoles, U.S. Pat. No. 2,732,301; mineral acids; carboxylic acids, such as maleic acid, dichloroacetic acid, trichloroacetic acid and salicylic acid, sulfonic and phosphoric acids, and various dyes, such as cyanine (including carbocyanine), merocyanine, diarylmethane, thiazene, azine, oxazine, xanthenes, phthalein, acridine, azo, anthraquinone dyes and the like and mixtures thereof. The sensitizers preferred for use with the compounds of this invention are selected from pyrrole salts including selena-pyrrole salts and thiapyrrole salts, and cyanine dyes including carbocyanine dyes.

Where a sensitizing compound is employed with the binder and organic photoconductor to form a sensitized electrophotographic element, it is the normal practice to mix a suitable amount of the sensitizing compound with the coating composition so that, after thorough mixing, the sensitizing compound is uniformly distributed in the coated layer.

Other methods of incorporating the sensitizers or the effect of the sensitizers may, however, be employed consistent with the practice of this invention. In preparing the non-aggregate photoconductive layers, no sensitizing compound is required to give photoconductivity in the layers which contain the photoconductive substances, therefore, no sensitizing compound is required in a particular photoconductive layer. However, since relatively minor amounts of sensitizing compound are preferred.

The amount of sensitizing compound than can be added to a photoconductor-incorporating 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 sensitizing compound is added in a concentration range from about 0.001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizing compound is added to the coating composition in an amount by weight from about 0.005 to about 5.0 percent by weight of the total coating composition.

Preferred binders for use in preparing the present non-aggregate photoconductive layers are film-forming, hydrophobic polymeric binders having fairly high dielectric strength and good electrical insulating properties.

Typical of these materials are:

I. Natural resins including gelatin, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxyl ethyl cellulose, carboxy methyl cellulose, carboxy methyl hydroxy ethyl cellulose, etc.;

II. Vinyl resins including

a. A polyvinyl esters such as a vinyl acetate resin, a copolymer of vinyl acetate and propionic acid, a copolymer of vinyl acetate with an ester of vinyl alcohol and a higher aliphatic carboxylic acid such as lauric acid or stearic acid, polyvinyl stearate, a copolymer of vinyl acetate and maleic acid, a poly(vinylhaloacrylate) such as poly(vinyl-halomethacrylate-covinyl acetate), a terpolymer of vinyl butyral with vinyl alcohol and vinyl acetate, etc.;

b. Vinyl chloride and vinylidene chloride polymers such as a poly(vinylchloride), a copolymer of vinyl chloride and vinyl isobutyl ether, a copolymer of vinylidene chloride and acrylonitrile, a terpolymer of vinyl chloride, vinyl acetate and vinyl alcohol, poly(vinylidene chloride) a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride, a copolymer of vinyl chloride and vinyl acetate, etc.;

c. Styrene polymers such as polystyrene, a nitrated polystyrene, a copolymer of styrene and monoiso-butyl maleate, a copolymer of styrene with methacrylic acid, a copolymer of styrene and butadiene, a copolymer of dimethylethacconate and styrene, polymethylstyrene, etc.;

d. Methacrylic acid ester polymers such as a poly(alkylmethacrylate), etc.;

e. Polyolefins such as chlorinated polyethylene, chlorinated polypropylene, polyisobutylene, etc.;

f. Poly(vinyl acetalts) such as poly(vinyl butyral), etc.; and

g. Poly(vinyl alcohol);

III. Polycarbonates including

a. A polyester of 1,3-disulfobenzene and 2,2-bis(4-hydroxyphenyl)propane;

b. A polyester of diphenyl-p,p'-disulphonic acid and 2,2-bis(4-hydroxyphenyl)propane;

c. A polyester of 4,4'-dicarboxyethyl ether and 2,2-bis(4-hydroxyphenyl)propane;

d. A polyester of 2,2-bis(4-hydroxyphenyl)propane and fumaric acid;

e. Polyester of pentaerythritol and phthalic acid;

f. Resinous terpene polybasic acid;

g. A polyester of phosphoric acid and hydroquinone;

h. Polyphosphites;

i. Polyester of neopentylglycol and isophthalic acid;

j. Polycarbonates including polythio-carbonates such as the polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane;

k. Polyester of isophthalic acid, 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane and ethylene glycol;

l. Polyester of terephthalic acid, 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane and ethylene glycol;

m. Polyester of ethylene glycol, neopentyl, glycol, terephthalic acid and isophthalic acid;

n. Polyamides;

o. Ketone resins; and

p. Phenol-formaldehyde resins;

IV. Silica resins;

V. Alkyd resins including styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, etc.;

VI. Polyamides;

VII. Paraflin; and

VIII. Mineral waxes.

Solvents useful for preparing coating compositions containing the photoconductors of the present invention can include a wide variety of organic solvents for the components of the coating composition.

Typical solvents include:

1. Aromatic hydrocarbons such as benzene, naphthalene, etc., including substituted aromatic hydrocarbons such as toluene, xylen, or methylene, etc.;

2. Ketones such as acetone, 2-butanone, etc.;

3. Halogenated aliphatic hydrocarbons such as methyl chloride, chloroform, ethylene chloride, etc.;

4. Ethers including cyclic ethers such as tetrahydrofuran, ethylether;

5. Mixtures of the above.

In preparing the non-aggregate-containing photoconductive coating compositions of the present invention
useful results are obtained where the photoconductor is present in an amount equal to at least about 0.1 weight percent of the coating composition. The upper limit in the amount of photoconductive material present can be widely varied to at least 90% by weight in accordance with usual practice.

Suitable supporting materials on which the photoconductive layers of this invention can be coated 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 or conventional photographic film bases such as cellulose acetate, polystyrene, etc. Such conducting materials as nickel can be vacuum deposited 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 or vacuum deposited on the support. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. No. 3,243,833 by Trevoy, issued Apr. 12, 1966. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester 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. Pat. No. 3,007,901 by Minsk, issued Nov. 7, 1961 and U.S. Pat. No. 3,262,807 by Stermann et al., issued July 26, 1966.

Coating thicknesses of the photoconductive composition on the support can vary widely. Normally, a coating in the range of about 10 microns to about 300 microns 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 50 microns to about 150 microns before drying, although useful results can be obtained outside of this range. The resultant dry thickness of the coating is preferably between about 2 microns and about 50 microns, although useful results can be obtained with a dry coating thickness between about 1 and about 200 microns.

After the photoconductive elements prepared according to the method of this invention have been dried, they can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the xerographic process. In a process of this type, an electrophotographic element is held in the dark and given a blanket electrostatic charge by placing it under a corona discharge. This uniform charge is retained by the layer because of the substantial dark 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 imagewise exposure to light by means of a conventional exposure operation such as, for example, by a contact printing technique, or by lens projection of an image, and the like, to thereby form a latent electrostatic image in the photoconductive layer. Exposing the surface in this manner forms a pattern of electrostatic charge by virtue of the fact that light energy striking and the photoconductor causes the electrostatic charge in the light struck areas to be conducted away from the surface in proportion to the intensity of the illumination in a particular area. The charge pattern produced by exposure is then developed or transferred to another surface and developed there, i.e., either the charged or uncharged areas rendered visible, by treating with a medium comprising electrostatically responsive particles having optical density. The developing electrostatically responsive particles can be in the form of a dust, i.e., powder, or a pigment in a resinous carrier, i.e., toner. A preferred method of applying such toner to a latent electrostatic image for solid area development is by the use of a magnetic brush. Methods of forming and using a magnetic brush toner applicator are described in the following U.S. Pat.: U.S. Pat. No. 2,786,439 by Young, issued Mar. 26, 1957; U.S. Pat. No. 2,786,640 by Giaino, issued Mar. 26, 1957; U.S. Pat. No. 2,786,441 by Young, issued Mar. 26, 1957; U.S. Pat. No. 2,874,063 by Greig, issued Feb. 17, 1959. Liquid development of the latent electrostatic image may also be used. In liquid development, the developing particles are carried to the image-bearing surface in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature, for example, U.S. Pat. No. 2,907,674 by Metcalfe et al., issued Oct. 6, 1959. In dry developing processes, the most widely used method of obtaining a permanent record is achieved by selecting a developing particle which has as one of its components a low-melting resin. Heating the powder image then causes the resin to melt or fuse into or on the element. The powder is, therefore, caused to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the electrostatic charge image formed on the photoconductive layer can be made to a second support such as paper which would then become the final print after development and fusing. Techniques of the type indicated are well known in the art and have been described in the literature such as in "RCA Review" Vol. 15 (1954) pages 469-484. The following examples are included for a further understanding of this invention.

Preparation of Photoconductors

The photoconductive materials used in the compositions of the invention may be prepared by known methods of chemical synthesis. Generally, the compounds used herein are prepared by reacting any of various dialkylarylphosphonates with an appropriate aldehyde in the presence of a strong base to give the desired olefin product. By this procedure, the reaction of diphenylaminobenzaldehyde or 4-di-p-tolylamino)benzaldehyde with an appropriate bisphosphonate and two equivalents of sodium methoxide in dimethylformamide solution is used to prepare the disteryl compounds I-VI listed in Table 1 hereinafter. For purposes of illustration the specific reaction procedure used to prepare compound V of Table 1 is as follows:

To a solution of 6.1 g of tetraethyl 4,6-dimethyl-m-xyleneidiphosphonate and 2.0 g of sodium methoxide in 50 ml of dimethylformamide is added dropwise at room temperature 9.0 g of 4-di-p-tolylaminobenzaldehyde in 50 ml of dimethylformamide; an exotherm to 40°C occurs. A solid separates
after several minutes and the mixture is stirred overnight at room temperature. The mixture is poured onto 100 g of ice, and the yellow solid is collected, washed with 50 ml of water and air-dried to give 10.5 g of crude product, m.p. 91°-102°C. Two recrystallizations from dimethyl-formamide gives 4.1 g of compound V if the form of yellow crystals, m.p. 211°-215°C.

The other photoconductive compounds of Table 1 are prepared by a similar procedure.

EXAMPLE 1

In this example aggregate and homogeneous organic photoconductive compositions of the present invention are compared to the somewhat similar photoconductors described in Merril, U.S. Pat. No. 3,653,887 to demonstrate the unexpected improvement in 100 volt positive toe speed provided by the photoconductive compositions of the present invention. A set of four different photoconductive compositions coated on a conductive film support are tested for each photoconductor, three homogeneous photoconductive compositions, i.e. Nos. 1-3 below, and one aggregate composition, i.e. No. 4 below, the type described in Light, U.S. Pat. No. 3,615,414. The formulation of the compositions used in this example is as follows:

No. 1: 78.4 weight percent polyester binder, 20 weight percent photoconductor, 1.6 weight percent of the sensitizer 4-(n-butyl amino)-2-(4-methoxy phenyl) benzo [b] pyrylim pyrroldione perchlorate
No. 2: 79.2 weight percent polyester binder, 0.8 weight percent of the sensitizer Rhodamine B
No. 3: 80.0 weight percent polyester binder, 20.0 weight percent polyester resin, no sensitizer
No. 4: 78.0 weight percent polycarbonate binder, 20.0 weight percent photoconductor, and 2.0 weight percent of the sensitizer 4-p-dimethylamino-phenyl-2,6-diphenyl-pyrylim pyrchlorate

The above four compositions are tested using two different photoconductors, A and B. Photoconductor A is a compound of the type described in U.S. Pat. No. 3,653,887 and has the formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{N} & \quad \text{O} \\
\text{CH}_3 & \quad \text{C=CH} \\
\text{CN} & \quad \text{C} \\
\text{CN} & \quad \text{N} \\
\text{CH}_3 & \quad \text{O}
\end{align*}
\]

Photoconductor B is compound II of Table 1 of the present invention. The following data is obtained:

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>RELATIVE ELECTRICAL H &amp; D SPEED (+100 VOLT TOE)</td>
</tr>
<tr>
<td>Photocouductor</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
</tbody>
</table>

*arbitrarily assigned a relative speed value of 100 for this photocouductor

The relative positive 100 volt toe speeds in Table 3 are measured as described in Example 4 hereinafter. As shown in Table 3, the relative 100 volt positive toe speeds of photocouductor B of the present invention are substantially higher than prior art photocouductor A.

EXAMPLE 2

This example illustrates the blue sensitivity of aggregate photoconductive compositions of the present invention. The following aggregate photoconductive composition consisting of:

- 3.92 g of polycarbonate resin
- 0.08 g of 4-p-dimethylaminophenyl-2,6-diphenylthiopyrimidine perchlorate
- 26.8 ml of dichloromethane

is prepared as follows:

The formulation is made up by a seed-shear technique which consists of the preparation of two stock solutions.

SOLUTION I

- 3.92 g of polycarbonate resin
- 0.08 g of 4-p-dimethylaminophenyl-2,6-diphenylthiopyrimidine perchlorate
- 26.8 ml of dichloromethane

The above dope is sheared in a Waring Blender for 30 minutes at 70°F.

SOLUTION II

- A dye solution is prepared consisting of 0.03 g of 4-p-dimethylaminophenyl-2,6-diphenylthiopyrimidine perchlorate and 10.2 ml of dichloromethane.

A dope containing these solutions is prepared as follows:

- 7.7 g of Solution I
- 4.5 g of Solution II
- 0.25 g of photocouductor II of Table 1
- 0.25 g of Lexan 145

The above-described dope is then coated on a conductive poly(ethylene terephthalate) support to provide a resultant aggregate photoconductive element. Wedge spectrograms of this aggregate photoconduc-
charging exhibit a sensitivity minimum at 460 nm, thereby indicating the absence of blue sensitivity possessed by these photoconductive elements.

**EXAMPLE 3**

To illustrate the advantage of using the organic photoconductive material of the present invention in combination with various inorganic photoconductors, three different photoconductive compositions are made having the composition shown below as follows:

Photoconductor II of Table 1 is combined with tetragonal PbO in a polyester binder and coated on a conductive support to yield the following data shown in Table 4:

<table>
<thead>
<tr>
<th>Binder</th>
<th>Inorganic Photoconductor</th>
<th>Photoconductor II of Table 1</th>
<th>Relative Electrical H and D Speed (Sh/100 Volt Toe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84% by weight</td>
<td>PbO 16% by weight</td>
<td>Absent</td>
<td>0/0</td>
</tr>
<tr>
<td>95% by weight</td>
<td>Absent</td>
<td>5% by weight</td>
<td>2.5/0</td>
</tr>
<tr>
<td>79% by weight</td>
<td>PbO 16% by weight</td>
<td>5% by weight</td>
<td>9/0/5</td>
</tr>
</tbody>
</table>

* arbitrarily assigned a value of one for this example

**EXAMPLE 4**

Each of photoconductors I–VI of Table 1 are used to form both homogeneous and aggregate photoconductive compositions of the invention. The homogeneous photoconductive compositions prepared in this example are prepared containing about 80% by weight of a polyester binder, about 0.8% by weight of the sensitizer 2,6-bis(p-ethylphenyl)-4-(p-n-amidoxophenyl)-thiapyrylm perchlorate, and about 19% by weight of each of photoconductors I–VI. The aggregate photoconductive compositions prepared in this example contain about 80% by weight of polycarbonate binder, about 2.0% by weight of the sensitizer 2,6-diphenyl-4-(p-dimethylaminophenyl)-thiapyrylm perchlorate, and about 18% by weight of each of photoconductors I–VI of Table 1. Relative H and D positive and negative shoulder and 100 toe volt electrical speeds are measured for each of these photoconductive compositions as shown in Table 5.

In Examples 1–4 of the present application Relative H & D Electrical Speeds are reported. The relative H & D electrical speeds measure the speed of a given photoconductive material relative to other materials typically within the same test group of materials. The relative speed values are not absolute speed values. However, relative speed values are related to absolute speed values. The relative electrical speed (shoulder or toe speed) is obtained simply by arbitrarily assigning a value, Ro, to one particular absolute shoulder or toe speed of one particular photoconductive material. The density gray scale. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential V₀ to some lower potential V the exact value of which depends upon the amount of exposure in meter-candle-seconds received by the area. The result of these measurements are then plotted on a graph of surface potential V vs. log exposure for each step, thereby forming an electrical characteristic curve. The electrical or electrophotographic speed of the photoconductive composition can them be expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed selected value. The actual positive or negative shoulder speed is the numerical expression of 10 divided by the exposure in meter-candle-seconds required to reduce the initial surface potential V₀ to some value equal to V₀ minus 100. This is referred to as the 100 volt shoulder speed. Sometimes it is desirable to determine the 50 volt shoulder speed and, in that instance, the exposure used is that required to reduce the surface potential to V₀ minus 50. Similarly, the actual positive or negative toe speed is the numerical expression of 10 divided by the exposure in meter-candle-seconds required to reduce the initial potential V₀ to an absolute value of 100 volts. Again, if one wishes to determine the 50 volt toe speed, one merely uses the exposure required to reduce V₀ to an absolute value of 50 volts. An apparatus useful for determining the electrophotographic speeds of photoconductive compositions is described in Robinson et al., U.S. Patent No. 3,449,658, issued June 10, 1969.

### Table 4

<table>
<thead>
<tr>
<th>Binder</th>
<th>Inorganic Photoconductor</th>
<th>Photoconductor II of Table 1</th>
<th>Relative Electrical H and D Speed (Sh/100 Volt Toe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84% by weight</td>
<td>PbO 16% by weight</td>
<td>Absent</td>
<td>0/0</td>
</tr>
<tr>
<td>95% by weight</td>
<td>Absent</td>
<td>5% by weight</td>
<td>2.5/0</td>
</tr>
<tr>
<td>79% by weight</td>
<td>PbO 16% by weight</td>
<td>5% by weight</td>
<td>9/0/5</td>
</tr>
</tbody>
</table>

* arbitrarily assigned a value of one for this example

### Table 5

<table>
<thead>
<tr>
<th>Photoconductor</th>
<th>Homogeneous (Hom)</th>
<th>Aggregate (Ag)</th>
<th>Relative Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shoulder</td>
<td>Toe</td>
<td>Shoulder</td>
</tr>
<tr>
<td>I</td>
<td>Hom</td>
<td>100*</td>
<td>15.7</td>
</tr>
<tr>
<td>II</td>
<td>Ag</td>
<td>987</td>
<td>67</td>
</tr>
<tr>
<td>III</td>
<td>Hom</td>
<td>111</td>
<td>14</td>
</tr>
<tr>
<td>IV</td>
<td>Ag</td>
<td>987</td>
<td>251</td>
</tr>
<tr>
<td>V</td>
<td>Hom</td>
<td>100</td>
<td>3.9</td>
</tr>
<tr>
<td>VI</td>
<td>Ag</td>
<td>86</td>
<td>13.3</td>
</tr>
<tr>
<td>V</td>
<td>Hom</td>
<td>2036</td>
<td>148.7</td>
</tr>
<tr>
<td>V</td>
<td>Ag</td>
<td>47</td>
<td>9.9</td>
</tr>
<tr>
<td>VI</td>
<td>Hom</td>
<td>2506</td>
<td>156.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.13</td>
</tr>
</tbody>
</table>

* arbitrarily assigned a value of 100 for positive speed tabulation
** arbitrarily assigned a value of 100 for negative speed tabulation
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photoconductive composition comprising an electrically insulating polymeric binder and a photoconductor an organic compound having the formula

\[ R_2 \xrightarrow{\text{N-Ar}_1-\text{CH=CH-Ar}_2-\text{CH=CH-Ar}_3-\text{N}} R_3 \]

wherein

\( R_1, R_2, R_3, R_4, R_5, \) and \( R_6 \) are each selected from the group consisting of an aryl radical and an alkyl radical,

\( \text{Ar}_1 \), and \( \text{Ar}_2 \) are each selected from the group consisting of an unsubstituted phenyl radical and a substituted phenyl radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, and \( \text{Ar}_5 \) is an aromatic radical containing 4-14 carbon atoms in the aromatic ring thereof, said aromatic radical being a member selected from the group consisting of unsubstituted carboxyclic aromatic radicals, unsubstituted sulfur heterocyclic aromatic radicals having a sulfur atom as the only heteroatom thereof, and said carboxyclic or said sulfur heterocyclic aromatic radicals having an alkyl, aryl, alkoxy or halogen substituent.

2. A photoconductive composition as described in claim 3 wherein said composition contains an inorganic photoconductive compound.

3. A photoconductive composition comprising an electrically insulating binder, an organic photoconductive compound, and an amount of sensitizer effective to sensitize said composition, said photoconductive compound having the formula

\[ R_1 \xrightarrow{\text{N-Ar}_1-\text{CH=CH-Ar}_2-\text{CH=CH-Ar}_3-\text{N}} R_3 \]

wherein

\( R_1, R_2, R_3, R_4, \) and \( R_5 \) are each selected from the group consisting of an aryl radical and an alkyl radical,

\( \text{Ar}_1 \), and \( \text{Ar}_2 \) are each selected from the group consisting of an unsubstituted phenyl radical and a substituted phenyl radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, and

\( \text{Ar}_2 \) is an unsubstituted carboxyclic aromatic radical or a substituted carboxyclic aromatic radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, said aromatic radical containing 4-14 carbon atoms in the aromatic ring thereof.

4. A photoconductive composition as described in claim 3 wherein \( R_1, R_2, R_3, \) and \( R_4 \) are each aryl radicals and \( \text{Ar}_2 \) is a phenyl radical or an alkyl-substituted phenyl radical containing 1 to about 4 carbon atoms in said alkyl substituents.

5. A photoconductive composition as described in claim 3 wherein said photoconductor is selected from the group consisting of 4-(4-diphenylamino)-2',3',5',6'-tetramethyl-4'-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-4'-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-2',2',4',4'-dimethyl-5'-[4-(di-p-tolylamino)styrlyl]stilbene; 9,10-bis[4-(di-p-tolylamino)styryl]anthracene; and 1,4-bis[4-N-ethyl-N-p-tolylaminostyryl]benzene.

6. A photoconductive composition as described in claim 3 wherein said composition contains photoconductive lead oxide.

7. An aggregate photoconductive composition comprising a continuous binder phase containing (a) dissolved therein greater than about 15 percent by weight of one or more organic photoconductors and (b) dispersed therein a particulate co-crystalline complex of (1) a dye selected from the group consisting of a 2,4,6-substituted pyrylum dye salt and a 2,4,6-substituted thiaprylum dye salt and (2) a carbonate polymer having an alkyldiene diarylene moiety in a recurring unit, each of said organic photoconductors having the formula

\[ R_1 \xrightarrow{\text{N-Ar}_1-\text{CH=CH-Ar}_2-\text{CH=CH-Ar}_3-\text{N}} R_3 \]

wherein

\( R_1, R_2, R_3, R_4, \) and \( R_5 \) are each selected from the group consisting of an aryl radical and an alkyl radical,

\( \text{Ar}_1 \), and \( \text{Ar}_2 \) are each selected from the group consisting of an unsubstituted phenyl radical and a substituted phenyl radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, and

\( \text{Ar}_5 \) is an unsubstituted carboxyclic aromatic radical or a substituted carboxyclic aromatic radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, said aromatic radical containing 4-14 carbon atoms in the aromatic ring thereof.

8. An aggregate photoconductive composition as described in claim 7 wherein \( R_1, R_2, R_3, \) and \( R_4 \) are each phenyl radicals or alkyl-substituted phenyl radicals and \( \text{Ar}_2 \) is a phenyl radical or an alkyl-substituted phenyl radical, said alkyl substituents having 1 or 2 carbon atoms.

9. An aggregate photoconductive composition as described in claim 7 wherein said organic photoconductor is selected from the group consisting of 4-diphenylamino-4'-(4-diphenylamino)styryl]stilbene; 4-di-(p-tolylamino)-4'-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-2',2',3',5',6'-tetramethyl-4'-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-2',2',4',4'-dimethyl-5'-[4-(di-p-tolylamino)styrlyl]stilbene; 9,10-bis[4-(di-p-tolylamino)styryl]anthracene; and 1,4-bis[4-N-ethyl-N-p-tolylaminostyryl]benzene.

10. In an electrophotographic element comprising a conductive support and a photoconductive layer coated over said support, the improvement wherein said photoconductive layer comprises the photoconductive composition of claim 2.

11. In an electrophotographic element comprising a conductive support and a photoconductive layer coated over said support, the improvement wherein said photoconductive layer comprises the photoconductive composition of claim 6.

12. In an electrophotographic process wherein an electrostatic charge pattern is formed on a photocon-
ductive element comprised of an electrically conductive support having coated thereover a layer of a photoconductive composition, the improvement wherein said photoconductive composition is as described in claim 2.

13. An aggregate photoconductive composition comprising a continuous binder phase containing (a) dissolved therein greater than about 15% by weight of one or more organic photoconductors and (b) dispersed therein a particulate co-crystalline complex of (1) a dye selected from the group consisting of thiapyrylum, selena pyrylum, and pyrylum dye salts and (2) a carbonate polymer having an alkylidene diarylene moiety in a recurring unit, each of said organic photoconductors having the formula

\[ R_1^{-N} - A_{R_2} - CH = CH - A_{R_3} - CH = CH - A_{R_4} - N - R_3 \]

wherein \( R_1, R_2, R_3, \) and \( R_4 \) are each selected from the group consisting of an aryl radical and an alkyl radical, \( A_{R_2} \) and \( A_{R_3} \) are each selected from the group consisting of an unsubstituted phenyl radical and a substituted phenyl radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, and \( A_{R_2} \) is an aromatic radical containing 4-14 carbon atoms in the aromatic ring thereof, said aromatic radical being a member selected from the group consisting of unsubstituted carbocyclic aromatic radicals, unsubstituted sulfur heterocyclic aromatic radicals having a sulfur atom as the only heteroatom thereof, and said carbocyclic or said sulfur heterocyclic aromatic radicals having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent.
UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,873,312
DATED : March 25, 1975
INVENTOR(S) : Lawrence E. Contois and Louis J. Rossi

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 30, "differential" should read ---differential---;
Column 2, line 2, "element" should read ---elements---;
line 42, "distyryl-containing" should read ---distyryl-containing---; line 48, "distyryl-containing" should read ---distyryl-containing---; line 56, "distyryl-containing" should read ---distyryl-containing---.

Column 3, line 25, "a.," should read ---al.,---; line 49, "pheny" should read ---phenyl---.

Column 11, line 5, "BB" should read ---22---.

Column 13, line 7, "thiazene" should read ---thiazine---;
Column 14, lines 64-65, "tertrahydrofuran" should read ---tetrahydrofuran---.

Column 16, line 1, "and" should be deleted.

Column 18, line 14, that part of formula reading "dimethyl-amine" should read ---dimethylamino---.

Column 20, line 34, "them" should read ---then---; line 35, "terms" should read ---terms---; line 51, "abosolute" should read ---absolute---.
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,873,312
DATED : March 25, 1975
INVENTOR(S) : Lawrence E. Contois and Louis J. Rossi

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

(Continued)
Column 21, line 33, "3" should read ---1---; last line, that part of formula reading "[4-(4-(di" should read ---[4-(di---.

Column 22, line 61, "2" should read ---1---; line 66, "6" should read ---7---.

Column 23, line 11, "2" should read ---1---.

Signed and Sealed this thirtieth Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks