United States Patent [19]

Contois et al.

[11] **3,873,311**

[45] **Mar. 25, 1975**

[54] **AGGREGATE PHOTOCONDUCTIVE COMPOSITIONS AND ELEMENTS CONTAINING A STYRYL AMINO GROUP CONTAINING PHOTOCONDUCTOR**

[75] Inventors: **Lawrence E. Contois,** Webster; **Louis J. Rossi,** both of Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

[22] Filed: **Feb. 19, 1974**

[21] Appl. No.: **443,655**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 357,441, May 4, 1973, abandoned.

[52] **U.S. Cl.** **96/1.6,** 96/1.5

[51] **Int. Cl.** **G03g 5/06**

[58] **Field of Search** 96/1.5, 1.6

[56] **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	Gramza et al.	96/1.6
3,615,414	10/1971	Light	96/1.6
3,615,415	10/1971	Gramza	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.
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[57] **ABSTRACT**

An improved "aggregate" photoconductive composition and electrophotographic elements containing the same are prepared using from 0.1 to less than about 15 weight percent of 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.

11 Claims, No Drawings

AGGREGATE PHOTOCONDUCTIVE COMPOSITIONS AND ELEMENTS CONTAINING A STYRYL AMINO GROUP CONTAINING PHOTOCONDUCTOR

This application is a continuation-in-part of U.S. Ser. No. 357,441, filed May 4, 1973, now abandoned. Cross reference is also made to copending Contois and Rossi, U.S. Ser. No. 443,657, filed concurrently herewith and entitled "Photoconductive Composition and Elements Containing Same."

FIELD OF THE INVENTION

This invention relates to electrophotoraphy and in particular to photoconductive compositions and elements.

DESCRIPTION OF THE PRIOR ART

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 an insulating material whose electrical resistance varies with the amount of incident electromagnetic radiation it receives during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge, generally in the dark after a suitable period of dark adaptation. It is then exposed to a pattern of actinic radiation 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 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 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. Deposited marking material can then be either permanently 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 employoed in the manufacture of electrophotographic elements. For example, vapors of selenium and vapors of selenium alloys deposited on a suitable support and particles of photoconductive zinc oxide held in a resinous, film-forming binder have found wide application in present-day decument copying processes.

Since the introduction of electrophotography, a great many organic comounds 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 organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Among these organic photoconductors are the triphenylamines as described in U.S. Pat. No. 3,180,730 issued Apr. 27, 1965, and other aromatic ring compounds such as those described in British Pat. No. 944,326 dated Dec. 11, 1963; U.S. Pat. No. 3,549,358 issued Dec. 22, 1970 and U.S. Pat. No. 3,653,887 issued Apr. 4, 1972.

Optically clear organic photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements 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 effective prediction, and therefore selection of the particular compounds exhibiting the desired electrophotographic properties.

A high speed "heterogeneous" or "aggregate" multiphase photoconductive system was developed by William A. Light which overcomes many of the problems of the prior art. This aggregate photoconductive composition (as it is referred to hereinafter) is the subject matter of U.S. Pat. No. 3,615,414 issued Oct. 26, 1971 and is also described in Gramza et al. U.S. Pat. No. 3,732,180 issued May 8, 1973. 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 therewith. The degree of such enhancement is, however, variable, depending on the particular organic photoconductor so used.

SUMMARY OF THE INVENTION

In accord with the present invention there is provided an aggregate photoconductive composition containing at least two different organic photosensitive components in solid solution with the continuous phase of the multiphase aggregate composition, one of said components being a non-blue light absorbing organic photoconductor and one of said components being an amount within the range of from about 0.1 to less than about 15 weight percent based on the dry weight of said composition of 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.

The improved aggregate photoconductive compositions of the present invention offer a number of advantages. Among others, it has been noted that these compositions provide especially useful reusable photoconductive compositions because of their ability to resist electrical fatigue upon being subjected to a large number of repetitive electrophotographic imaging cycles.

In addition, the improved aggregate photoconductive compositions of the invention offer an unexpected enhancement in blue light sensitivity.

Moreover, it has also been found that aggregate photoconductive compositions containing the distyryl-containing aromatic compounds used in the present invention exhibit improved temperature stability. Accordingly, the improved aggregate photoconductive compositions of the invention containing these compounds are useful over a wider range of operating temperatures.

In addition, it has been found that the above advantages provided by the improved aggregate photoconductive compositions of the present invention are generally obtained without any substantial deleterious affect of the totality of electrophotographic properties which cooperate to produce a useful photoconductive composition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "non-blue light absorbing organic photoconductor" as used herein is defined as a photoconductor which exhibits little or no light absorption in the spectral range extending from about 400 to 500 nm. Such photoconductors are typically transparent to visible light and therefore colorless; or if colored, these materials are a color other than yellow, a yellow coloration of course, indicating that blue light is being absorbed. Visible light is defined herein as radiation within the 400–700 nm. region of the spectrum.

The precise mechanism(s) occurring in the improved aggregate photoconductive compositions of the invention has not been conclusively established and therefore the present invention should not be limited by any specific theory. However, a number of obserations have been made relating to the photoconductive compositions of the invention and are presented herein to provide a better understanding of the invention.

In the first place, the photoconductive mechanism(s) which is believed to occur in the improved aggregate photoconductive compositions of the invention is considered to be different than that which normally occurs in conventional "homogeneous" organic photoconductive compositions. Such homogeneous compositions consist of an organic photoconductor such as a triphenylamine compound in solid solution with a polymeric binder. Typically, a sensitizer is also present in the composition. Photoconduction is believed to occur in a uniformly electrostatically charged homogeneous photoconductive composition as a result to exposure to radiation of the type to which the organic photoconductor is intrinsically sensitive (or to which the organic photoconductor is made sensitive by the addition of a sensitizer), thereby causing the generation of charge carriers within the organic photoconductor. These charge carriers are then transported through the photoconductive composition to a conductive layer where they are dissipated.

In the improved aggregate photoconductive compositions of the present invention charge carriers are believed to be generated in the photoconductive composition from within the particles of aggregate material contained therein. these particles of aggregate material are generally composed of a cocrystalline complex of an organic sensitizing dye, such as a pyrylium type dye, and a polymeric material, such as a polycarbonate, and are visible within the photoconductive composition with the aid of a microscope. These aggregate particles are thus dispersed as a discontinuous phase in the photoconductive composition and are not in a solid solution with the remainder of the composition. (Further detail relating to the preparation and composition of these aggrergate particles is set forth hereinafter.)

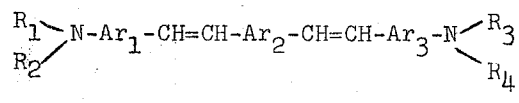
In accord with the invention one or more non-blue light absorbing organic photoconductor(s) is incorporated in solid solution with the continuous phase of the aggregate photoconductive composition of the invention. These materials may aid the above-described aggregate particles in the formation of charge carriers, and it is also believed that the organic photoconductor(s) plays a primary role in the transport of the charge carriers through the aggregate photoconductive composition. It has been shown, for example, that the photoconductivity, i.e. electrophotographic speed, of the compositions of the invention when exposed to a white light source is significantly increased by the addition of the organic photoconductor(s). Without the incorporation of one or more organic photoconductors, the white light speed of the composition is so low that the compositions of the present invention are unacceptable for use in conventional office copier applications.

The distyryl-containing aromatic compound contained in the aggregate photoconductive composition of the invention is used as a "fatigue reducer" and as a "temperature stabilizer." For example, the improved aggregate composition of the invention exhibit substantial improvement in resistance to electrical fatigue even when subjected to a large number of repetitive imaging cycles at relatively high ambient temperature conditions. In addition, although these distyryl-containing aromatic compounds are known to possess photoconductive properties (as described in the cross-referenced Contois and Rossi U.S. patent application Ser. No. 443,657, entitled "Photoconductive Composition and Elements Containing Same" filed concurrently herewith), these compounds are believed to act as a blue light sensitizer in the compositions of the present invention. That is, these compounds appear to absorb blue light and then, through some type of chemical, electronic or combined chemicalelectronic mechanism, intimately interest with the aggregate particles to generate charge carriers.

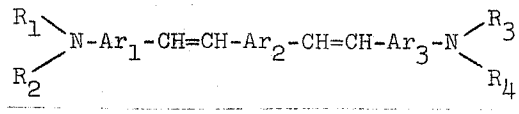
The precise reason(s) that the distyryl-containing aromatic compounds act as a blue sensitizer in the photoconductive composition of the invention are not completely understood. Although these distyryl-containing compounds do possess photoconductive properties and exhibit blue light absorption, these factors alone do not account for the enhanced blue sensitivity of the aggregate photoconductive compositions of the invention. This is readily demonstrated by the fact that certain known nitrosubstituted triphenylamine photoconductors which also exhibit blue light absorption, such as compounds similar to the nitrosubstituted triarylamines shown in U.S. Pat. No. 3,180,730, do not provide the above-described blue sensitization effect when substituted for the distyryl-containing compounds incorporated in the photoconductive compositions of the invention.

Similarly, the precise reason(s) that the distyryl-containing aromataic compounds improve the temperature stability and act as a fatigue reducer in the aggregate photoconductor composition of the invention is also not fully understood. However, here again it is known that molecularly much simpler nitro-substituted triphenylamine photoconductive compounds similar to those shown in U.S. Pat. No. 3,180,730 do not provide these advantages when substituted for the distyryl-containing aromatic compounds used in the aggregate-containing photoconductive compositions of the type described above.

The preferred distyryl-containing aromatic compounds used in the invention may be characterized by the following formula:



The preferred distyryl-containing aromatic compounds used in the invention may be characterized by the following formula:



wherein

R_1, R_2, R_3, and R_4, which can be the same or different, represent alkyl or aryl radicals including substituted alkyl and aryl radicals;

Ar_1 and Ar_3, 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, aryloxy, and halogen substituent; and

Ar_2 represents a carbocylic or sulfur heterocyclic, mononuclear or polynuclear, aromatic ring typically containing 4 to 14 carbon atoms in the ring such as phenyl, 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 Ar_1 and Ar_3.

Typically, R_1, R_2, R_3, and R_4 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. alkoxyalkyl e.g., ethoxypropyl, methoxybutyl, propoxymethyl, etc.,
   b. aryloxyalkyl e.g., phenoxyethyl, naphthoxymethyl, phenoxypentyl, etc.
   c. aminoalkyl, e.g., aminobutyl, aminoethyl, aminopropyl, etc.,
   d. hydroxyalkyl e.g., hydroxypropyl, hydroxyoctyl, etc.,
   e. aralkyl e.g., benzyl, phenethyl, etc.
   f. alkylaminoalkyl e.g., methylaminopropyl, methylaminoethyl, etc., and also including dialkylaminoalkyl e.g., diethylaminoethyl, dimethylaminopropyl, propylaminooctyl, etc.,
   g. arylaminoalkyl, e.g., phenylaminoalkyl, diphenylaminoalkyl, N-phenyl-N-ethylaminopentyl, N-phenyl-N-ethylaminohexyl, naphthylaminomethyl, etc.,
   h. nitroalkyl, e.g., nitrobutyl, nitroethyl, nitropentyl, etc.,
   i. cyanoalkyl, e.g., cyanopropyl, cyanobutyl, cyanoethyl, etc., and
   j. haloalkyl, e.g., chloromethyl, bromopenetyl, chlorooctyl, etc.,
   k. alkyl substituted with an acyl group having the formula



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 alkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc., aryloxy, e.g., phenoxy, naphthoxy, etc; or

2. an aryl group, e.g., phenyl, naphthyl, anthryl, fluoroenyl, etc., including a substituted aryl group such as
   a. alkoxyaryl, e.g., ethoxyphenyl, methoxyphenyl, propoxynaphthyl, etc.
   b. aryloxyaryl, e.g., phenoxyphenyl, phenoxynaphthyl, etc.
   c. aminoaryl, e.g. aminophenyl, aminonaphthyl, aminoanthryl, etc.
   d. hydroxyaryl, e.g., hydroxyphenyl, hydroxynaphthyl,
   e. biphenylyl,
   f. alkylaminoaryl, e.g., methylaminophenyl, methylaminonaphthyl, etc. and also including dialkylaminoaryl, e.g., diethylaminophenyl, dipropylaminophenyl etc.
   g. arylaminoaryl, e.g., phenylaminophenyl, diphenylaminophenyl, N-phenyl-N-etehylaminophenyl, naphthylaminophenyl, etc.
   h. nitroaryl e.g., nitrophenyl, nitronaphthyl, nitroanthryl, etc.,
   i. cyanoaryl, e.g., cyanophenyl, cyanonaphthyl, cyanoanthryl, etc.,
   j. haloaryl, e.g., chlorophenyl, bromophenyl, chloroanphthyl, etc.,
   k. alkaryl, e.g., tolyl, ethylphenyl, propylnaphthyl, etc., and
   l. aryl substituted with an acyl group having the formula



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

Typically, when either Ar_1 or Ar_3 represent a substituted phenyl radical the substituents on the phenyl radical are alkyl or aryl groups as defined above for R_1, R_2, R_3, R_4 or also any of the following:

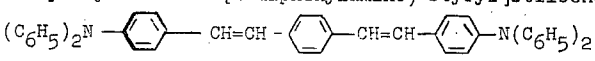
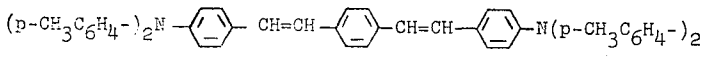
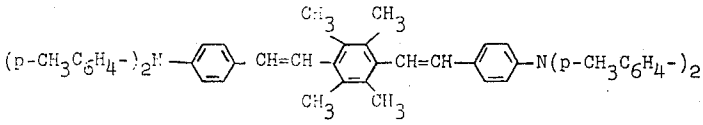
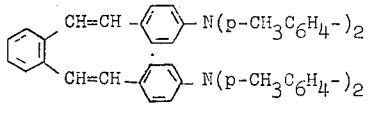
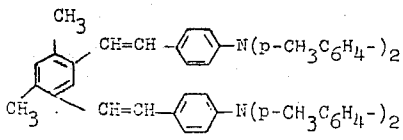
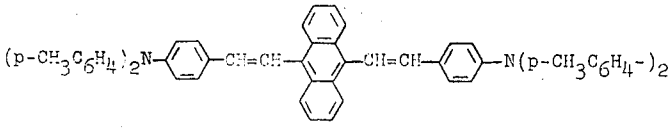
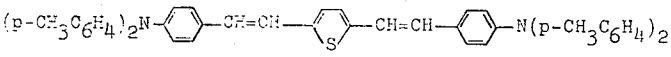
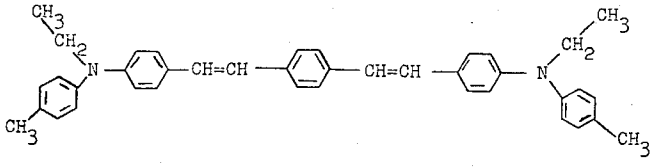
1. an alkoxy group having one to 18 carbon atoms, e.g., methoxy, ethoxy, propoxy, butoxy, etc.,
2. an aryloxy group e.g., phenoxy, naphthoxy, etc.; and
3. halogen such as chlorine, bromine, fluorine or iodine.

Typical compounds which belong to the general class of distyryl-containing aromatic compounds described

herein include the following materials listed in Table 1 below:

resistance to electricall fatigue and improved temperature stability.

TABLE 1

		Melting Point °C
(I)	4-Diphenylamino-4'-[4-diphenylamino) styryl]stilbene having the formula 	209-211°
(II)	4-Di-(p-tolylamino)-4'-[4-(di-p-tolylamino)styryl]stilbene having the formula 	216-220°
(III)	4-Di-(p-tolylamino)-2',3', 5',6'-tetramethyl-4'-[4-(di-p-tolylamino)-styryl]stilbene having the formula 	231-233°
(IV)	4-Di-(p-tolylamino)-2'-[4-(di-p- tolylamino)-styryl]stilbene having the formula 	106-108°
(V)	4-Di-(p-tolylamino)-2',4'-dimethyl-5'-[4-(di-p-tolylamino)styryl]stilbene having the formula 	211-215°
(VI)	9,10-Bis[4-(di-p-tolylamino)styryl]-anthracene having the formula 	288-290°
(VII)		———
(VIII)	1,4-Bis(4-N-ethyl-N-p-tolylaminostyryl)benzene having the formula 	204-206°

Compounds which below to the general class of distyryl-containing aromatic 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 Ar_1, Ar_2 and Ar_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. These compounds are preferred because aggregate compositions containing the same exhibit increased blue sensitivity and may also exhibit improved

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 elimi-

nates 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 above-described distyryl-containing compounds and one or more organic photoconductors in a suitable solvent to form an organic 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 view under magnification, although such 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.

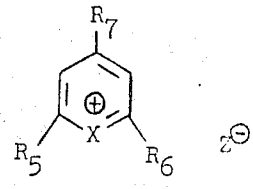
In general, the aggregate compositions formed as described herein are multiphase oroganic solids containing dye and polymer. The polymer forms an amorphous matarix or continuous phase which contains a discrete discontinuous phase as distinguished from a solution. The discontinuous phase is the aggregate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

Sensistizing 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:



wherein:

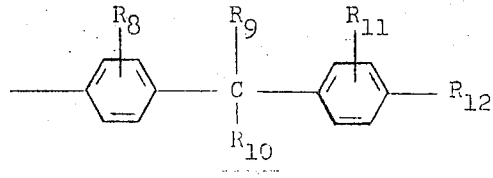
R_5 and R_6 can each be phenyl radicals, including substituted phenyl radicals having at least one substituent chosen from alkyl radicals of from 1 to about 6 carbon atoms and alkoxy radicals having from 1 to about 6 carbon atoms;

R_7 can be alkylamino-substituted phenyl radical having from 1 to 6 carbon atoms in the alkyl moiety, and including dialkylamino-substituted and haloalkylamino-substituted phenyl radicals;

X can abe an oxygen or a sulfer atom; and

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 alkylidene diarylene moiety in a recurring unit such as those linear polymers, including copolymers, containing the following moiety in a recurring unit:

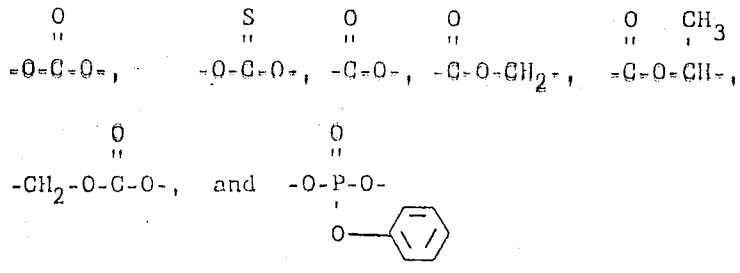


wherein:

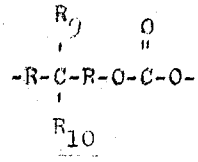
R_9 and R_{10}, when taken separately, can each be a hydrogen atom, an alkyl radical having from one to about 10 carbon atoms such as methyl, ethyl, isobutyl, hexyl, heptyl, octyl, nonyl, decyl and the like including substituted alkyl radicals such as trifluoromethyl, etc., and an aryl radical such as 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 R_9 and R_{10}, when taken together, can represent the carbon atoms necessary to complete a saturated cyclic hydrogen radical including cycloalkanes such as cyclohexyl and polycycloalkanes such as norbornyl, the total number of carbon atoms in R_9 and R_{10} being up to about 19;

R_8 and R_{11} can each be hydrogen, an alkyl radical of from 1 to about 5 carbon atoms, e.g., or a halogen such as chloro, bromo, iodo, etc.; and

R_{12} is a divalent radical selected from the following:



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



wherein:

each R is a phenylene radical including halo substituted phenylene radicals and alkyl substituted phenylene radicals; and R_9 and R_{10} 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 alkylidene 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. Pat. Nos. 2,999,750 by Miller et al., issued Sept. 12, 1961; 3,038,874 by Laakso et al., issued June 12, 1962; 3,038,879 by Laakso et al., issued June 12, 1962; 3,038,880 by Laakso et al., issued June 12, 1962; 3,106,444 by Laakso et al., issued Oct. 8, 1963; 3,106,545 by Laakso et al., issued Oct. 8, 1963; and 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 practicie of this invention:

Table 2

No.	Polymeric Material
1	poly(4,4'-isopropylidenediphenylene-co-1,4-cyclohexanylenedimethylene carbonate)
2	poly(ethylenedioxy-3,3'-phenylene thiocarbonate)
3	poly(4,4'-isopropylidenediphenylene carbonate-co-terephthalate)
4	poly(4,4'-isopropylidenediphenylene carbonate)
5	poly(4,4'-isopropylidenediphenylene thiocarbonate)
6	poly(4,4'-sec-butylidenediphenylene carbonate)
7	poly(4,4'-isopropylidenediphenylene carbonate-block-oxyethylene)
8	poly(4,4'-isopropylidenediphenylene carbonate-block-oxytetramethylene)
9	poly[4,4'-isopropylidenebis(2-methyl-phenylene)-carbonate]
10	poly(4,4'-isopropylidenediphenylene-co-1,4-phenylene carbonate)
11	poly(4,4'-isopropylidenediphenylene-co-1,3-phenylene carbonate)
12	poly(4,4'-isopropylidenediphenylene-co-4,4'-diphenylene carbonate)
13	poly(4,4'-isopropylidenediphenylene-co-4,4'-oxydiphenylene carbonate)
14	poly(4,4'-isopropylidenediphenylene-co-4,4'-carbonyldiphenylene carbonate)
15	poly(4,4'-isopropylidenediphenylene-co-4,4'-ethylenediphenylene carbonate)
16	poly[4,4'-methylenebis(2-methyl-phenylene)carbonate]
17	poly[1,1-(p-bromophenylethylidene)bis(1,4-phenylene)carbonate]

Table 2 — Continued

No.	Polymeric Material
18	poly[4,4'-isopropylidenediphenylene-co-4,4'-sulfonyldiphenylene) carbonate]
19	poly[4,4'-cyclohexanylidene(4-diphenylene) carbonate]
20	poly[4,4'-isopropylidenebis(2-chlorophenylene) carbonate]
21	poly(4,4'-hexafluoroisopropylidenediphenylene carbonate)
22	poly(4,4'-isopropylidenediphenylene 4,4'-isopropylidenedibenzoate)
23	poly(4,4'-isopropylidenedibenzyl 4,4'-isopropylidenedibenzoate)
24	poly[4,4'-(1,2-dimethylpropylidene)diphenylene carbonate]
25	poly[4,4'-(1,2,2-trimethylpropylidene)-diphenylene carbonate]
26	poly 4,4'-[1-(α-naphthyl)ethylidene]-diphenylene carbonate
27	poly[4,4'-(1,3-dimethylbutylidene)-diphenylene carbonate]
28	poly[4,4'-(2-norbornylidene)diphenylene carbonate]
29	poly[4,4'-(hexahydro-4,7-methanoindan-5-ylidene) diphenylene carbonate]

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 self-supporting 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 polyers can be incorporated in the vehicle, for example, to physical properties such as adhesion of the photoconductive layer to the support and the like. A list of various other polyers which may be used may be found in the publicaton *Research Disclosure*, Vol. No. 109, May, 1973, p. 63, in Paraphgram IV B of the article entitled "Electrophotographic elements, materials, and processes". The foregoing article is hereby incorporated herein by reference thereto. 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 layer of the invention can also be further sensitized by the addition of effective amounts of other known sensitizing compounds to exhibit improved electrophotosensitivity.

In accord with the invention, the above-described distyryl-containing aromatic compounds are combined with one or more non-blue light-absorbing organic photoconductors to form the improved aggregate photoconductive compositions of the invention. The non-blue light absorbing organic photoconductive materials are advantageously incorporated by dissolving these materials in the organic solvent dope used in coating the improved aggregate photoconductive compositions of the invention. As a result these organic photoconductive materials are in solid solution with the continuous polymer phase of the multiphase structure of the resultant aggregate photoconductive composition. Incorporation of these organic photoconductors in the aggregate compositions of the invention advantageously results in significantly increasing the white light

electrical speed of the aggregate composition.

Especially useful organic photoconductors which exhibit little or no blue light absorption and which may be incorporated in the improved aggregate compositions of the invention include non-blue light absorbing materials selected from the following classes of photoconductors: Arylamine photoconductors including substituted and unsubstituted arylamines, diarylamines, nonpolymeric triarylamines and polymeric triarylamines such as those described in Fox, U.S. Pat. No. 3,240,597, issued Mar. 15, 1966 and Klupfel et al. U.S. Pat. No. 3,180,730 issued Apr. 27, 1965; and polyarylalkane photoconductors of the types described in Noe et al. U.S. Pat. No. 3,274,000, issued Sept. 20, 1966, Wilson, U.S. Pat. No. 3,542,547, issued Nov. 24, 1970; Seus et al. U.S. Pat. No. 3,542,544, issued Nov. 24, 1970; and in Rule U.S. Pat. No. 3,615,402, issued Oct. 26, 1971. Of course, if desired, other non-blue light absorbing organic photoconductors such as those selected from the various classes of organic photoconductors disclosed in Light, U.S. Pat. No. 3,615,414 (hereby incorporated herein by reference thereto) may also be incorporated in the aggregate compositions of the invention.

The amount of the above-described distyryl-containing compound incorporated into the aggregate photoconductive compositions and elements of the invention should be less than about 15 weight percent based on the total dry weight of the resultant aggregate photoconductive compositions.

Particularly useful results are obtained where the aggregate compositions of the invention contains 15 to about 40 percent by weight of one or more non-blue light absorbing organic photoconductors and as an additive an amount of the distyryl-containing aromatic compound within the range of from about 0.1 to about 10 weight percent based on the total dry weight of the resultant composition. As the amount of the distyryl-containing aromatic compound is increased beyond the 15 weight percent level specified herein, the absorportion and photoconductive properties of the compound begin to have a substantial effect on the resultant photoconductive composition. In addition, the enhancement in electrical fatigue resistance (sometimes referred to in the art as charge regeneration) provided in the present invention by use of a relatively small amount of the distyryl-containing compound is impared as very large amounts of the distyryl-containing aromatic compound are usecd (i.e. amounts on the order of about 25 weight percent or more). It has been found that certain especially useful embodiments of the present invention which contain in solid solution with the continuous phase of the aggregate photoconductive composition (a) 25 weight percent or more of one or more non-blue light absorbing organic photoconductors and (b) less than 15 weight percent, preferably 5 to 10 weight percent, of the distyryl-containing aromatic compounds described herein provide optimum reusable characteristics. That is, the small amount of the distyryl compound appears to function primarily as a fatigue reducer, temperature stabilizer, and blue light sensitizer for the particulate co-crystalline complex incorporated in the aggregate photocoductive composition as described previously herein and appears to have little or no deleterious effect on the photoresponse of the composition to visible light outside the blue region, i.e., light having a wavelength of from 500 to 700 nm.

As noted above, the amounts of the non-blue light absorbing organic photoconductors incorporated in the compositions of the invention which produce optimum results in the terms of electrical fatigue, speed, and temperature stability are usually within the range of from about 15 to about 40, preferably 25 to about 40, percent by weight based on the total dry weight of the resultant aggregate photoconductive composition. However, larger and somewhat smaller amounts of these photoconductors may also be used

Suitable supporting materials on which the aggregate 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. 3,245,833 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. Nos. 3,007,901 by Minsk, issued Nov. 7, 1961 and 3,262,807 by Sterman et al., issued July 26, 1966.

Coating thickness 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 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 charge or uncharged areas rendered visible, by treatment 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. Nos.: 2,786,439 by Young, issued Mar. 26, 1957; 2,786,440 by Giaimo, issued Mar. 26, 1957; 2,786,441 by Young, issued Mar. 26, 1957; 2,874,063 by Greig, issed 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 Distyryl-Containing Aromatic Compounds

This distytyl-containing aromatic compounds used in the compositions of the invention may be prepared by known methods of chemical synthesis. Specifically, 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 p-diphenylaminobenzaldehyde or 4-di-(p-tolylamino)-benzaldehyde with an appropriate bis-phosphonate and two equivalents of sodium methoxide in dimethylformamide solution is used to prepare the distyryl compounds I–VIII listed in Table 1 hereinbefore.

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-xylylenediphosphonate 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 in the form of yellow crystals, m.p. 211°–215°C.

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

EXAMPLE 1

Using aggregate formulation methods as described earlier herein, a series of aggregate organic photoconductive compositions are prepared containing two different organic photoconductors. The basic dry formulation of each aggregate photocoductive composition tested is as follows: Bisphenol A polycarbonate (56% by weight) purchased from General Electric Co.) + total amount of organic photoconductor (40–30% by weight) + total amount of 4-di-p-tolylamino-4'[4-di-p-tolylaminostyryl]-stilbene (0–10 % by weight) + 4-(4-dimethylaminophenyl-2,6-diphenyl thiapyrylium fluoroborate (3.4% by wt.) + 4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenyl thiapyrylium fluoroborate (.6% by wt.). Each aggregate composition is prepared as follows:

4-(4-Dimethylaminophenyl)-2,6-diphenyl thiapyrylium fluoroborate (0.17 g) and 4-(4-dimethylaminophenyl)-2-(4-ethoxyphenyl)-6-phenyl thiapyrylium fluoroborate (0.03 g) are dissolved in 15 mls. of dichloromethane. Three grams of bisphenol A polycarbonate are then dissolved in this solution and to this dope is added 2.0 grams (total) of organic photoconductor and 4-di-p-tolylamino-4'-[4-di-p-tolylaminostyryl]-stilbene. After allowing the dope to stand overnight 12.5 mls. of dichloromethane is added and the resulting dope is hand coated on a nickel coated conductive support to obtain a dry coating thickness of 9μ. Significant increases especially in blue speeds are observed when 4-di-p-tolylamino-4'-[4-di-p-tolylaminostyryl]-stilbene is combined with conventional organic photoconductors as shown in Table 3.

In this example 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 relative shoulder or toe speed, Rn, of any other photoconductive material, *n*, relative to this value, *Ro*, may then be calculated as follows: $Rn, = (A_n)(Ro/Ao)$ wherein *An* is the absolute electrical speed of material *n*, *Ro* is the speed value arbitrarily assigned to the first material, and *Ao* is the absolute electrical speed of the first material. The absolute H & D electrical speed, either the shoulder (SH) or toe speed, of a material may be determined as follows: The material is electrostatically charged under, for example, a corona source until

the surface potential, as measured by an electrometer probe, reaches some suitable initial value V_0, typically about 600 volts. The charged element is then exposed to 3000°K tungsten light source through a stepped 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 V_0 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 results 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 then 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 10^4 divided by the exposure in meter-candle-seconds required to reduce the initial surface potential V_0 to some value equal to V_0 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 V_0 minus 50. Similarly, the actual positive or negative toe speed is the numerical expression of 10^4 divided by the exposure in meter-candle-seconds required to reduce the initial potential V_0 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 V_0 to an absolute value of 50 volts. An apparatus useful for determining the eletrophotographic speeds of photoconductive compositions is described in Robinson et al., U.S. Pat. No. 3,449,658, issued June 10, 1969.

TABLE 3

Weight percent of 4-di-p-tolylamino-4'-[4-di-p-tolyl-aminostyryl]-stilbene	Weight percent of Conventional Photoconductors (tri-p-tolylamine)	Relative + 100 Volt Toe Speeds	
		Tungsten Light Source	Blue Light Source
0	40	100*	100*
5	35	121	200
10	30	136(Vo=490)	200
Weight percent of 4-di-p-tolylamino-4'-[4-di-p-tolyl-aminostyryl]-stilbene	Weight percent of (Bis[4-diethylamino] tetraphenylmethane)		
0	40	100*	100*
5	35	125	141
10	30	140	155

*arbitrarily assigned a speed value of 100 within each column and within each series.

EXAMPLE 2

Three transparent photoconductive films containing aggregate photoconductive compositions are prepared similar to certain of the films of Example 1. The electrophotographic sensitivity of these films (evaluated as the inverse sensitivity of the exposure required to discharge the film from 500 v. to 100 v.) is determined as a function of wavelength for all electrophotographic modes, positive and negative surface charging and front and rear exposure. In addition, absorption spectra for each of the three films is recorded and evaluated.

Each of the three films tested is identical except for the particular aggregate photoconductive composition used in each film. Each of the aggregate photoconductive compositions of the three films contains a particulate co-crystalline complex of a thiapyrylium dye and Lexan polycarbonate as a discontinuous phase dispersed in a continuous polymer phase composed of Lexan polycarbonate. The particular thiapyrylium dye used in each of the three films is 2,6-diphenyl-4-(p-dimethylaminophenyl) thiapyrylium fluoroborate and the total amount of dye contained in each composition is 3% by weight based on the total dry weight of the aggregate photoconductive composition used in each film. The total amount of Lexan polycarbonate contained in each of the photoconductive compositions used in the films is 57% by weight.

A. The remaining 40% by weight of the aggregate photoconductive composition of Film No. 1 (which is a control outside the scope of the present invention) is composed entirely of the organic photoconductor 4,-4'bis-diethylaminotetraphenylmethane (TPM) which is in solid solution with the Lexan polycarbonate contained in the continuous phase of the phtotconductive composition of Film No. 1.

B. The remaining 40% of the aggregate photoconductive composition of Film No. 2 (which is within the scope of the present invention) is composed of 30% by weight of TPM and 10% by weight of compound II of Table 1 of the present application as an additive. The TPM and compound II used in Film No. 2 is in solid solution with the Lexan polycarbonate contained in the continuous phase of the photoconductive composition of Film No. 2.

C. The remaining 40% of the aggregate photoconductive composition of Film No. 3 (which is also a control outside the present invention) is composed of 30% by weight of TPM and 10% by weight of ditolyl-p-nitrophenylamine (DTN). DTN is a yellow appearing prior art compound known to have photoconducitve properties and also known to absorb blue light. The TPM and DTN used in Film No. 3 is in solid solution with the Lexan polycarbonate contained in the continuous phase of the photoconductive composition of Film No. 3.

The absorption spectra of Film Nos. 1-3 reveals that

Film No. 1 possesses a "window" to blue light, i.e., visible light having a wavelength of from about 400–500 nm. That is, Film No. 1 exhibits very little absorption of blue light. Film No. 1, however, readily absorbs visible light having a wavelength within the spectral range of from about 500–700 nm. Film Nos. 2 and 3 exhibit an absorption spectra similar to Film No. 1 with respect to visible light having a wavelength within the spectral range of from about 500–700 nm. However, in contrast to Film No. 1, Film Nos. 2 and 3 also absorb blue light so that the blue "window" of Film No. 1 does not appear in either Film No. 2 or 3.

The electrophotographic sensitivity of each of Film Nos. 1–3 reveals that both controls, i.e., Film Nos. 1 and 3, exhibit rather poor electrophotographic sensitivity when exposed to blue light but exhibit good and substantially similar electrophotographic sensitivity to visible light having a wavelength extending from about 500–700 nm. Film No. 2 of the present invention, however, exhibits good electrophotographic sensitivity to blue light. Film No. 2 also exhibits good electrophotographic sensitivity to light having a wavelength extending from about 500–700 nm. Except for the increased electrophotographic sensitivity to blue light exhibited by Film No. 2 of the present invention, the electrophotographic sensitivity of Film Nos. 1–3 to light having a wavelength within the range of from 500–700 nm is quite similar.

The results of the tests shown in this example indicate that the blue sensitization capability of aggregate photoconductive compositions containing compound II of Table 1 (which is representative of the distyryl-containing aromatic compounds of the present invention) is a unique effect and cannot be obtained simply by substituting other known blue absorbing organic photoconductors, such as DTN, for compound II.

Of perhaps even greater significances are the additional test findings that when temperature stability and electrical fatique tests are run on Film Nos. 1–3, the results show that Film No. 2 (which contains as an additive one of the distyryl-containing aromatic compounds used in the present invention) exhibits substantially better resistance to electrical fatique and substantially better temperature than either Film No. 1 or 3. For example, Film No. 2 appears to provide good reusable electrophotographic imaging characteristics similar to room temperature (i.e. about 28°C) imaging characteristics up to temperatures approaching 65°–70°C. In contrast, the electrophotographic imaging characterisics of Film Nos. 1 and 3 begins to fall off quite noticeably at a temperature of about 55°C in comparison to the normal room temperature (about 28°C) imaging characteristics provided by these same films.

EXAMPLE 3

To further illustrate certain of the preferred aggregate photoconductive compositions of the present invention, a 500 cycle electrical regeneration test and an evaluation of relative white light speed is performed on a series of three aggregate photoconductive elements to determine optimum amounts of the distyryl-containing aromatic compound to be incorporated therein for use as an additive. These elements are prepared having coated thereon an aggregate photoconductive composition containing the following materials expressed in weight precent; Bisphenol A polycarbonate (56%) purchased from General Electric Co. under the trademark Lexan 145; 4-(4-dimethylaminophenyl)-2,6-diphenyl thiapyrylium hexafluorophosphate sensitizing dye salt (4%); and the remaining 40% of each composition is as shown in Table 4. Each of the three aggregate photoconductive elements is prepared by coating the above-described aggregate composition on a conductive film support to obtain a dry coating thickness of about 9 microns. The aggregate photoconductive compositions coated on each of the three elements tested has an identical composition as indicated above except as shown in Table 4 hereinafter.

The evaluation of white light speed used in this example is carried out by subjecting each of the three aggregate photoconductive compositions for equal times to an identical source of white light radiation using a lens system which is equivalent to a photographic *f*-number of *f*/11. Before the *f*/11 light exposure, each of the three compositions is given in the dark a uniform negative charge level of −500 volts. Accordingly, the composition which exhibits the highest white light speed in this test is the composition which most completely discharges to the zero charge level.

Each cycle of the 500 cycle electrical charge fatigue test carried out on these three aggregate elements comprises the steps of (a) subjecting the element to an initial uniform charge, Vo, in the dark of −500 volts, imagewise exposing the uniformly negatively charged surface of the element to white light using a Xenon flashlamp to form an imagewise charge pattern on the surface of the element corresponding to the original light image pattern, and erasing the imagewise charge pattern by a uniform light exposure of the charge-bearing surface of the element. Since only the electrical properties of each element are being tested no development of the charge pattern or transfer thereof is carried out. After completing 500 repetitions of the foregoing cycle, the ability of the photoconductive element to accept completely the intitial charge, Vo, of −500 volts is measured. If the element retains its ability to accept completely the −500 volt charge, no electrical fatigue is measurable; therefore the difference in initial charge acceptance capability, ΔVo as set forth in Table 4, is zero. If after completing the 500 repetitions of the fatigue test, the photoconductive element is no longer capable of completely accepting the full initial charge of −500 volts, the amount of charge it does accept is measured and the difference between this value and the initial −500 volts, i.e. ΔVo, is calculated and apperas under the column ΔVo in Table 4. As indicated in Table 4 an element containing an aggregate photoconductive composition which has only a conventional photoconductor known to be useful in aggregate photoconductive materials (i.e. bis(4-diethylamino)tetraphenyl methane) exhibits a ΔVo of −25 volts indicating that it definitely experiences significant electrical fatique when subjected to repeated re-charging and re-exposure. This fatigue characteristic is, of course, disadvantageous for any such photoconductive element contemplated for use as a reusable photoconductive element. In contrast, as Table 4 clearly shows, when an amount of compound II of Table 1 is added to the aggregate photoconductive elements tested in this example, the amount of electrical fatigue as measured by the foregoing 500 cycle test is substantially reduced — ultimately no measurable fatique is obtained as the amount of compound II of Table 1 added to the aggregate photoconductive compositions tested in this example is in-

creased. However, as is also shown in Table 1, the element which exhibits little or no measureable fatique also shows a white light speed loss relative to the elements containing lesser amounts of compound II. Thus in accord with the invention, the amount of the distyryl-containing compound which should be added to obtain an optimum reusable aggregate photoconductive composition should be less than about 15 weight percent.

TABLE 4

ELECTRICAL FATIGUE TEST RESULTS
Remaining 40% by Weight of Aggregate
Compositions Used in Elements of Example 3

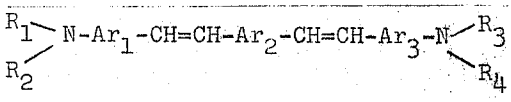
Weight % of Conventional Photoconductor*	Weight % of Compound II of Table 1	ΔVo	f/11 white light speed (volts)
40 (outside scope of present invention	0	−25	−70
30	10	−15	−65
20 (outside scope of present invention)	20	0	−215

*bis(4-diethylamino) tetraphenylmethane

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. An aggregate photoconductive composition comprising (a) a continuous electrically insulating polymer phase, said polymer having an alkylidene diarylene moiety in a recurring unit, (b) a discontinuous phase comprising a co-crystalline complex of (i) a pyrylium salt selected from the group consisting of thiapyrylium, selenapyrylium, and pyrylium dye salts and (ii) a carbonate polymer having an alkylidene diarylene moiety in a recurring unit, said discontinuous phase dispersed in said continuous phase, (c) at least one non-blue light absorbing organic photoconductor in solid solution with the continuous phase of said composition, and (d) from about 0.1 to about 15 weight percent based on the dry weight of said composition of a compound having the formula

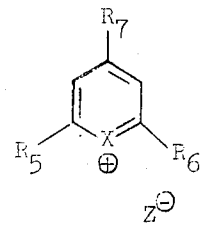


wherein

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

Ar_1 and Ar_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 Ar_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.

2. A photoconductive composition as described in claim 1 wherein said pyrylium salt has the formula:



wherein:

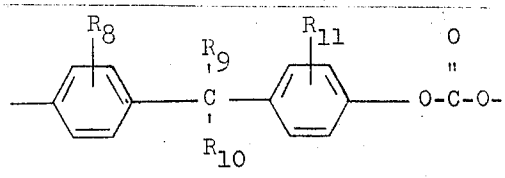
R_5 and R_6 are selected from the group consisting of phenyl and substituted phenyl having at least one substituent selected from the group consisting of an alkyl radical of from 1 to about 6 carbon atoms and an alkoxy radical of from 1 to about 6 carbon atoms;

R_7 is an alkylamino-substituted phenyl radical having from 1 to about 6 carbon atoms in the alkyl moiety;

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

Z^- is an anion.

3. A photoconductive composition as described in claim 1 wherein said carbonate polymer contains the following moiety in a recurring unit:

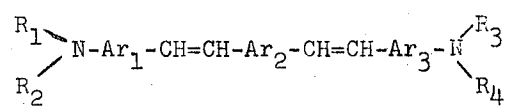


wherein:

each of R_9 and R_{10}, when taken separately, is selected from the group consisting of a hydrogen atom, an alkyl radical of from 1 to about 10 carbon atoms, and a phenyl radical, and R_9 and R_{10}, when taken together, are the carbon atoms necessary to form a cyclic hydrocarbon radical, the total number of carbon atoms in R_9 and R_{10} being up to 19; and

R_8 and R_{11} are each selected from the group consisting of hydrogen, alkyl radicals of from 1 to about 5 carbon atoms, alkoxy radicals of from 1 to about 5 carbon atoms and a halogen atom.

4. An aggregate photoconductive composition comprising (a) a continuous electrically insulating carbonate polymer phase, said polymer having an alkylidene diarylene moiety in a recurring unit, (b) a discontinuous phase comprising a co-crystalline complex of (i) a 2,4,6-substituted thiapyrylium dye salt and (ii) a carbonate polymer having an alkylidene diarylene moiety in a recurring unit, said discontinuous phase dispersed in said continuous phase, (c) from about 25 to about 40 weight percent based on the dry weight of said composition of at least one non-blue light absorbing organic photoconductor in solid solution with the continuous phase of said composition, and (d) from about 5 to about 10 weight percent based on the dry weight of said composition of a compound having the formula



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,

Ar_1 and Ar_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

Ar_2 is an unsubstituted carbocyclic aromatic radical containing 4–14 carbon atoms in the aromatic ring thereof or a substituted carbocyclic aromatic radical containing 4–14 carbon atoms in the aromatic ring thereof, said substituted aromatic radical having an alkyl, aryl, alkoxy, aryloxy, or halogen substituent, said compound in solid solution with the continuous phase of said composition.

5. An aggregate photoconductive composition as described in claim **4** wherein R_1, R_2, R_3, and R_4 are each phenyl radicals or alkyl-substituted phenyl radicals and Ar_2 is a phenyl radical or an alkyl-substituted phenyl radical, said alkyl substituents having 1 or 2 carbon atoms.

6. An aggregate photoconductive composition as described in claim **4** wherein said compound 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′, 3′, 5′, 6′-tetramethyl-4′-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-2′-[4-(di-p-tolylamino)styryl]stilbene; 4-di-(p-tolylamino)-2′,4′-dimethyl-5′-[4-(di-p-tolylamino)styryl]-stilbene; and 1,4-bis(4-N-ethyl-N-p-tolylaminostyryl)benzene.

7. An aggregate photoconductive composition as described in claim **4** wherein said organic photoconductor is a polyarylalkane photoconductor or an arylamine photoconductor.

8. An aggregate photoconductive composition as described in claim **4** wherein said organic photoconductor is a polyarylalkane photoconductor.

9. 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 **1.**

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 **4.**

11. In an electrophotographic process wherein an electrostatic charge pattern is formed on a photoconductive element comprised of an electrically conducting support having coated thereover a layer of a photoconductive composition, the improvement wherein said photoconductive composition is a composition as described in claim **4.**

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,873,311

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 3, line 54, "these" should read ---These---.

Column 4, line 37, "interest" should read ---interact---; line 58, "aromataic" should read ---aromatic---.

Column 5, line 65, "bromopenetyl" should read ---bromopentyl---.

Column 6, line 20, after "phenoxyphenyl," ---naphthoxyphenyl,--- should be inserted; line 25, after "hydroxynaphthyl,", ---hydroxyanthryl, etc.--- should be added; line 33, that part of formula reading "etehylaminophenyl" should read ---ethylaminophenyl---; lines 38-39, "chloroanphthyl" should read ---chloronaphthyl---; line 50, after "including", ---substituted--- should be inserted.

Column 7, line 56, "below" should read ---belong---.

Column 8, line 64, "this" should read ---This---.

Column 9, line 19, "oroganic" should read ---organic---.

Column 10, line 22, "abe" should read ---be---; line 22, "sulfer" should read ---sulfur---; line 53, "hydrogen" should read ---hydrocarbon---.

Column 11, line 29, "3,106,444" should read ---3,106,544---.

Column 12, line 15, that part of formula reading "poly 4,4'" should read ---poly{4,4'---; line 33, "polyers" should read ---polymers---; line 34, before "physical", ---alter--- should be inserted; line 37, "polyers" should read ---polymers---.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,873,311

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 13, lines 40-41, "absorportion" should read ---absorption---.

Column 15, line 51, "distytyl-containing" should read ---distyryl-containing---.

Column 18, lines 21-22, that part of formula reading "4,-4'bis" should read ---4,4'-bis---.

Column 20, line 49, "apperas" should read ---appears---.

Column 23, line 27, that part of formula reading "tolylamino)2',3',5',6'" should read ---tolylamino)-2',3',5',6'---.

Signed and Sealed this

sixth Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks