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Fox

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[45] **Oct. 23, 1973**

[54] **ALKYLAMINOAROMATIC ORGANIC PHOTOCONDUCTORS**

[75] Inventor: **Charles J. Fox**, Rochester, N.Y.

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

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[21] Appl. No.: **197,758**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 42,441, June 1, 1970, abandoned, which is a continuation-in-part of Ser. No. 834,984, June 20, 1969, abandoned.

[52] **U.S. Cl.** **96/1.5**, 96/1.6, 260/568, 260/571, 260/573, 260/576, 260/578

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

[58] **Field of Search** ..... 96/1 R, 1 PC, 1.5; 252/501

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Primary Examiner—Roland E. Martin, Jr.
Attorney—Robert W. Hampton et al.

[57] **ABSTRACT**

Alkylaminoaromatic compounds and vinylaminoaromatic compounds are useful as organic photoconductors in electrophotographic systems.

8 Claims, 2 Drawing Figures

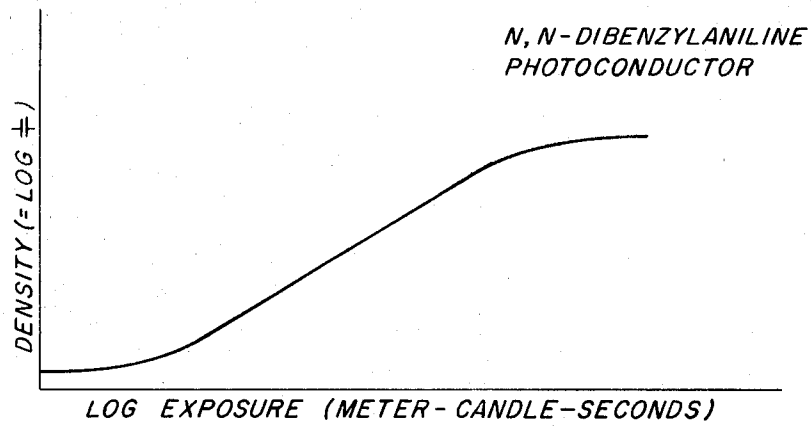


FIG. 1

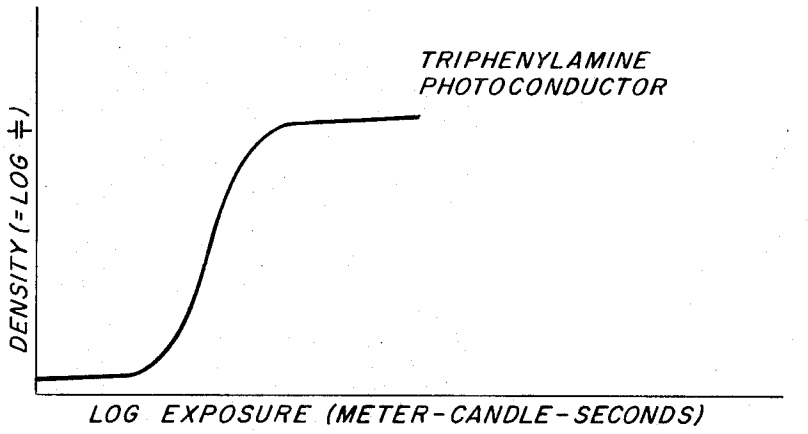


FIG. 2

CHARLES J. FOX
INVENTOR.
BY F. L. Denson
ATTORNEY

ALKYLAMINOAROMATIC ORGANIC PHOTOCONDUCTORS

This is a continuation-in-part application based on U.S. Ser. No. 42,441, filed June 1, 1970, now abandoned, which is a continuation-in-part of Ser. No. 834,984, filed June 20, 1969, now abandoned.

This invention relates to electrophotography, and in particular to photoconductive compositions and elements, and to processes for their use.

The process of xerography, as disclosed by Carlson in U.S. Pat. No. 2,297,691, employs an electrophotographic element comprising a support material bearing a coating of a normally insulating material whose electrical 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 latent image can be transferred to a second element and developed there.

Various photoconductive insulating g—employed 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 materials have been copying applications.

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 organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions.

Typical of these organic photoconductors are the triphenylamines and the triarylmethane leuco bases. Optically clear 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 unusual flexibility in equipment design. Such compositions, when coated as a film or layer on a suitable support, also yield an element which is reusable; that is, it can be used to form subsequent images after residual toner from prior images has been removed by transfer and/or cleaning. Most of the photoconductors that have been investigated thus far have been employed in films which are used in processes where high contrast is necessary such as in document-copying applications. These photoconductors and films are generally not suitable in applications requiring low contrast such as in continuous tone reproductions.

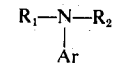
It is therefore an object of this invention to provide novel photoconductive compositions containing a class of photoconductors which have low contrast characteristics.

It is a further object of the invention to provide electrophotographic elements containing novel photoconductive compositions having low contrast characteristics.

It is another object of this invention to provide an improved electrophotographic process using elements containing novel photoconductive compositions.

These and other objects of this invention are accomplished by employing an N-alkylaminoaromatic compound or an N-vinylaminoaromatic compound as a photoconductor. Photoconductive elements containing these compounds have good low contrast characteristics and as such, are very suitable for use in continuous tone reproduction. In comparison, photoconductive elements containing other photoconductors such as triarylamine are characterized by high contrast and are generally unsuitable for continuous tone reproductions.

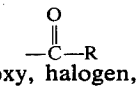
The preferred N-alkylaminoaromatic photoconductors of this invention are characterized by the following formula:



wherein

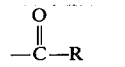
R_1 can be any of the following groups:

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, hydroxymethyl, etc.,
   - *e.* aralkyl, e.g., benzyl, phenylethyl, etc.,
   - *f.* alkylaminoalkyl, e.g., methylaminopropyl, methylaminoethyl, etc., and also including dialkylaminoalkyl, e.g., diethylaminoethyl, dimethylaminopropyl, propylaminooctyl, etc.,
   - *g.* haloaminoalkyl,e.g., dichloroaminoethyl, N-chloro-N-ethylaminopropyl, bromoaminohexyl, etc.,
   - *h.* arylaminoalkyl, e.g., phenylaminoalkyl, diphenylaminoalkyl, N-phenyl-N-ethylaminopentyl, N-phenyl-N-chloroaminohexyl, naphthylaminomethyl,
   - *i.* nitroalkyl, e.g., nitrobutyl, nitroethyl, nitropentyl, etc.,
   - *j.* cyanoalkyl, e.g., cyanopropyl, cyanobutyl, cyanoethyl, etc.,
   - *k.* haloalkyl, e.g., chloromethyl, bromopentyl, chlorooctyl, etc.,
   - *l.* alkyl substituted with an acyl group having the formula



wherein R is hydroxy, halogen, e.g., chlorine, bromine, etc., 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, loweralkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc., aryloxy, e.g., phenoxy, naphthoxy, etc.;

2. an aryl group, e.g., phenyl, naphthyl, anthryl, fluorenyl, etc., including a substituted aryl group such as
   - *a.* alkoxyaryl, e.g., ethoxyphenyl, methoxyphenyl, propoxynaphthyl, etc.,
   - *b.* aryloxyaryl, e.g., phenoxyphenyl, naphthoxyphenyl, phenoxynaphthyl, etc.,
   - *c.* aminoaryl, e.g., aminophenyl, aminonaphthyl, aminoanthryl, etc.,
   - *d.* hydroxyaryl, e.g., hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc.,
   - *e.* biphenylyl,
   - *f.* alkylaminoaryl, e.g., methylaminophenyl, methylaminonaphthyl, etc. and also including dialkylaminoaryl, e.g., diethylaminophenyl, dipropylaminophenyl, etc.,
   - *g.* haloaminoaryl, e.g., dichloroaminophenyl, N-chloro-N-ethylaminophenyl, bromoaminophenyl, etc.,
   - *h.* arylaminoaryl, e.g., phenylaminophenyl, diphenylaminophenyl, N-phenyl-N-ethylaminophenyl, N-phenyl-N-chloroaminophenyl, naphthylaminophenyl, etc.,
   - *i.* nitroaryl, e.g., nitrophenyl, nitronaphthyl, nitroanthryl, etc.,
   - *j.* cyanoaryl, e.g., cyanophenyl, cyanonaphthyl, cyanoanthryl, etc.,
   - *k.* haloaryl, e.g., chlorophenyl, bromophenyl, chloronaphthyl, etc.,
   - *l.* aryl substituted with an acyl group having the formula

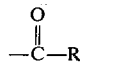


wherein R is hydroxy, halogen, e.g., chlorine, bromine, etc., hydrogen, aryl, e.g., phenyl, naphthyl, etc., amino including substituted amino, e.g., diloweralkylamine, lower alkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc., aryloxy, e.g., phenoxy, naphthoxy, etc., lower alkyl having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

   - *m.* alkaryl, e.g., tolyl, ethylphenyl, propylnaphthyl, etc.;

3. a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus, e.g., cyclobutyl, cyclohexyl, cyclopentyl, etc., including a substituted cycloalkyl group such as
   - *a.* alkoxycycloalkyl, e.g., ethoxycyclohexyl, methoxycyclobutyl, propoxycyclohexyl, etc.,
   - *b.* aryloxycycloalkyl, e.g., phenoxycyclohexyl, naphthoxycyclohexyl, phenoxycyclopentyl, etc.,
   - *c.* aminocycloalkyl, e.g., aminocyclobutyl, aminocyclohexyl, aminocyclopentyl, etc.,
   - *d.* hydroxycycloalkyl, e.g., hydroxycyclohexyl, hydroxycyclopentyl, hydroxycyclobutyl, etc.,
   - *e.* arylcycloalkyl, e.g., phenylcyclohexyl, phenylcyclobutyl, etc.,

   - *f.* alkylaminocycloalkyl, e.g., methylaminocyclohexyl, methylaminocyclopentyl, etc., and also including dialkylaminocycloalkyl, e.g., diethylaminocyclohexyl, dimethylaminocyclobutyl, dipropylaminocyclooctyl, etc.,
   - *g.* haloaminocycloalkyl, e.g., dichloroaminocyclohexyl, N-chloro,N-ethylaminocyclohexyl, bromoaminocyclopentyl, etc.,
   - *h.* arylaminocycloalkyl, e.g., phenylaminocyclohexyl, diphenylaminocyclohexyl, N-phenyl-N-ethylaminocyclopentyl, N-phenyl-N-chloroaminocyclohexyl, naphthylaminocyclopentyl, etc.,
   - *i.* nitrocycloalkyl, e.g., nitrocyclobutyl, nitrocyclohexyl, nitrocyclopentyl, etc.,
   - *j.* cyanocycloalkyl, e.g., cyanocyclohexyl, cyanocyclobutyl, cycanocyclopentyl, etc.,
   - *k.* halocycloalkyl, e.g., chlorocyclohexyl, bromocyclopentyl, chlorocyclooctyl, etc.,
   - *l.* cycloalkyl substituted with an acyl group having the formula



wherein R is hydroxy, halogen, e.g., chlorine, bromine, etc., hydrogen, aryl, e.g., phenyl, naphthyl, etc., amino including substituted amino, e.g., diloweralkylamino, loweralkoxy having one to eight carbon atoms, e.g., butoxy, methoxy, etc., aryloxy, e.g., phenoxy, naphthoxy, etc., loweralkyl having one to eight carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc.;

4. a heterocyclic group including a substituted heterocyclic group containing five to six members in the hetero nucleus and including at least one sulfur, selenium, oxygen or nitrogen atom such as a thienyl group, e.g., a benzothienyl group, a dibenzothienyl group, etc., a pyrrolyl group, e.g., a nitropyrrolyl group, a pyrrolidinyl group, e.g., a prolyl group, a pyrrolinyl group, a benzopyrrolyl group, e.g., an indolyl group, a carbazolyl group, a furyl group, e.g., a furfuryl group, a benzofuryl group etc., a pyridyl group, e.g., a halopyridyl group, an aminopyridyl group, a hydroxypyridyl group, an alkyl pyridyl group, a nitropyridyl group, etc., a piperidyl group, a quinolyl group, an acridinyl group, a pyranyl group, a benzopyranyl group, a pyrazolyl group, oxazolyl group, thiazolyl group, etc.

R_2 can be any of the following 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, hydroxymethyl, etc.,
   - *e.* aralkyl, e.g., benzyl, phenylethyl, etc.,
   - *f.* alkylaminoalkyl, e.g., methylaminopropyl, methylaminoethyl, etc., and also including dialkylaminoalkyl, e.g., diethylaminoethyl, dimethylaminopropyl, propylaminooctyl, etc.,

g. haloaminoalkyl,e.g., dichloraminoethyl, N-chloro-N-ethylaminopropyl, bromoaminohexyl, etc.,

h. arylaminoalkyl, e.g., phenylaminoalkyl, diphenylaminoalkyl, N-phenyl-N-ethylaminopentyl, N-phenyl-N-chloroaminohexyl, naphthylaminomethyl,

i. nitroalkyl, e.g., nitrobutyl, nitroethyl, nitropentyl, etc.,

j. cyanoalkyl, e.g., cyanopropyl, cyanobutyl, cyanoethyl, etc.,

k. haloalkyl, e.g., chloromethyl, bromopentyl, chlorooctyl, etc.,

l. alkyl substituted with an acyl group having the formula



wherein R is hydroxy, halogen, e.g., chorine, bromine, etc., 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.;

2. a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus, e.g., cyclobutyl, cyclohexyl, cyclopentyl, etc., including a substituted cycloalkyl group such as

a. alkoxycycloalkyl, e.g., ethoxycyclohexyl, methoxycyclobutyl, propoxycyclohexyl, etc.,

b. aryloxycycloalkyl, e.g., phenoxycyclohexyl, naphthoxycyclohexyl, phenoxycyclopentyl, etc.,

c. aminocycloalkyl, e.g., aminocyclobutyl, aminocyclohexyl, aminocyclopentyl, etc.,

d. hydroxycycloalkyl, e.g., hydroxycyclohexyl, hydroxycyclopentyl, hydroxycyclobutyl, etc.,

e. arylcycloalkyl, e.g., phenylcyclohexyl, phenylcyclobutyl, etc.,

f. alkylaminocycloalkyl, e.g., methylaminocyclohexyl, methylaminocyclopentyl, etc., and also including dialkylaminocycloalkyl, e.g., diethylaminocyclohexyl, dimethylaminocyclobutyl, dipropylaminocyclooctyl, etc.,

g. haloaminocycloalkyl, e.g., dichloroaminocyclohexyl, N-chloro-N-ethylaminocyclohexyl, bromoaminocyclopentyl, etc.,

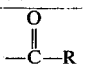
h. arylaminocycloalkyl, e.g., phenylaminocyclohexyl, diphenylaminocyclohexyl, N-phenyl-N-ethylaminocyclopentyl, N-pentyl-N-chloroaminocyclohexyl, naphthylaminocyclopentyl, etc.,

i. nitrocycloalkyl, e.g., nitrocyclobutyl, nitrocyclohexyl, nitrocyclopentyl, etc.,

j. cyanocycloalkyl, e.g., cyanocyclohexyl, cyanocyclobutyl, cyanocyclopentyl, etc.,

k. halocycloalkyl, e.g., chlorocyclohexyl, bromocyclopentyl, chlorocyclooctyl, etc.,

l. cycloalkyl substituted with an acyl group having the formula



wherein R is hydroxy, halogen, e.g., chlorine, bromine, etc., hydrogen, aryl, e.g., phenyl, naphthyl, etc., amino including substituted amino, e.g., diloweralkylamino, loweralkoxy 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.;

3. a vinyl group including a substituted vinyl group such as

a. alkoxyvinyl, e.g., ethoxyvinyl, methoxyvinyl, propoxyvinyl, etc.,

b. aryloxyvinyl, e.g., phenoxyvinyl, naphthoxyvinyl, etc.,

c. arylvinyl, e.g., styryl, naphthylvinyl, etc.,

d. alkylvinyl, e.g., propenyl, butenyl, etc.;

Ar represents an aryl group, e.g., phenyl, naphthyl, anthryl, fluorenyl, etc., including a substituted aryl group such as

a. alkoxyaryl, e.g., ethoxyphenyl, methoxyphenyl, propoxynaphthyl, etc.,

b. alkoxyaryl, e.g., ethoxyphenyl, naphthoxyphenyl, phenoxynaphthyl, etc.,

c. aminoaryl, e.g., aminophenyl, aminonaphthyl, aminoanthryl, etc.,

d. hydroxyaryl, e.g., hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc.,

e. biphenylyl,

f. alkylaminoaryl, e.g., methylaminophenyl, methylaminonaphthyl, etc., and also including dialkylaminoaryl, e.g., diethylaminophenyl, dipropylaminophenyl, etc.,

g. haloaminoaryl, e.g., dichloroaminophenyl, N-chloro-N-ethylaminophenyl, bromoaminophenyl, etc.,

h. arylaminoaryl, e.g., phenylaminophenyl, diphenylaminophenyl, N-phenyl,N-ethylaminophenyl, N-phenyl, N-chloroaminophenyl, naphthylaminophenyl, etc.,

i. nitroaryl, e.g., nitrophenyl, nitronaphthyl, nitroanthryl, etc.,

j. cyanoaryl, e.g., cyanophenyl, cyanonaphthyl, cyanoanthryl, etc.,

k. haloaryl, e.g., chlorophenyl, bromophenyl, chloronaphthyl, etc.,

l. aryl substituted with an acyl group having the formula



wherein R is hydroxy, halogen, e.g., chlorine, bromine, etc., hydrogen, aryl, e.g., phenyl, naphthyl, 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., loweralkyl having one to eight carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc.,

m. alkaryl, e.g., tolyl, ethylphenyl, propylnaphthyl, etc.

In the above formula at least one of R_1 and R_2 is preferably either an alkyl group, a vinyl group, or a cycloalkyl group.

Typical compounds which belong to the herein described general class of photoconductive materials include the following compounds listed in Table I below.

TABLE I

Photoconductor	Chemical Name
I	N,N-Dibenzylaniline
II	N-Benzyl-N-phenylaniline
III	N,N-Bis(cyclohexylmethyl)aniline
IV	N,N-Bis(cyclohexylethyl)aniline
V	N,N-Diphenethylaniline
VI	N,N-Diethylaniline

VII	1-Dimethylaminonaphthalene
VIII	1-Diethylaminonaphthalene
IX	N-Ethyl-N-phenylaniline
X	N-Ethyl-N-4-n-octylphenyl-4-n-octyaniline
XI	N,N'-Diethyl-N,N'-diphenylethylenediamine
XII	N-Cyclohexyl-N-phenylaniline
XIII	N-Ethyl-N-(2-phenoxyethyl)-3-methylaniline
XIV	1-Dimethylaminofluorene
XV	N-Benzyl-N-(4-pyridyl)aniline
XVI	N-Benzyl-N-(4-quinolyl)aniline
XVII	N-Styryl-N-phenylaniline

The advantages attributable to the use of the photoconductive materials described herein are further explained with reference to the drawings. The various configurations set forth in the drawings are not to scale and are included only for a better understanding of the invention. FIG. 1 is a plot of density (equal to the log of the reciprocal of the transmittance (T)) versus log exposure and the resultant S shaped curve obtained is known as either an "H and D curve" or "characteristic curve" for a photoconductive element containing N,N-dibenzylaniline as the photoconductor and Lexan 145 (a polycarbonate resin sold by General Electric Co.) as the binder, the photoconductor being 25 percent by weight of the photoconductive composition. This curve shows the relationship between increasing exposure and the increased density of the developed image. The curve is prepared by exposing a charged element containing one of the photoconductors described herein to a light source of given intensity through a 0.15 log E increment step tablet having 21 steps. After the exposure is completed, the resultant latent image on the surface of the photoconductive element is developed with an electrostatic toner in a manner to produce a reversal image. A densitometer is then used to measure the density of each of the developed steps. An analysis of the curve in FIG. I indicates that the film is responsive to small exposures as well as relatively larger exposures. The slope of the intermediate portion of the curve, γ, is such that intermediate tones are reproduced indicating that the film has a broad exposure range. An unexpected property of the photoconductors described herein is the relatively low γ of the "H and D curve."

For purposes of comparison, FIG. II represents the "H and D curve" of the "characteristic curve" for a photoconductive element containing a high contrast material such as a photoconductive composition containing a triphenylamine photoconductor and Lexan 145 as the binder, the photoconductor being 25 percent by weight of the photoconductive composition. An inspection of this curve reveals that the intermediate straight line portion of the curve has a very steep slope (i.e., high γ). The difference in exposure required to produce images having very low density and very high density is small. Thus, there is little or no opportunity for the reproduction of intermediate tones and the resultant image is generally either black or white. Materials having such high contrast characteristics are unsuitable for continuous tone reproductions.

Electrophotographic elements of the invention can be prepared with the photoconducting 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 material. Mixtures of the photoconductors described herein can be employed. Likewise, other 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 photoconductive layers of the invention can also 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 salts and selenapyrylium dye salts disclosed in VanAllan et al. U.S. Pat. No. 3,250,615; fluorenes, such as 7,12-dioxo-13-dibenzo(a,h) fluorene, 5,10-dioxo-4a,11-diazabenzo(b)fluorene, 3,13-dioxo-7-oxadibenzo(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. 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, and salicyclic acid; sulfonic and phosphoric acids; and various dyes, such as cyanine (including carbocyanine), merocyanine, diarylmethane, thiazine, azine, oxazine, xanthene, 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 pyrylium salts including selenapyrylium salts and thiapyrylium 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 element. Other methods of incorporating the sensitizer or the effect of the sensitizer may, however, be employed consistent with the practice of this invention. In preparing the photoconductive layers, no sensitizing compound is required to give photoconductivity in the layers which contain the photoconducting substances, therefore, no sensitizer is required in a particular photoconductive layer. However, since relatively minor amounts of sensitizing compound give substantial improvement in speed in such layers, the use of a sensitizer is preferred. The amount of sensitizer that 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 sensitizer is added in a concentration range from about 0.0001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount 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 photoconductive layers are film-forming, hydrophobic polymeric binders having fairly high dielectric strength

which are good electrically insulating, film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride-acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylenealkaryloxyalkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamides; polycarbonate; polythiocarbonates; poly(ethyleneglycol-co-bishydroxyethoxyphenyl propane terephthalate); copolymers of vinyl haloarylates and vinyl acetate such as poly(vinyl-m-bromobenzoate-covinylacetate); etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Pat. Nos. 2,361,019 and 2,258,423. Suitable resins of the type contemplated for use in the photoconductive layers of the invention are sold under such tradenames as Vitel PE-101, Cymac, Piccopale 100, Saran F-220, Lexan 105 and Lexan 145. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

Solvents useful for preparing coating compositions with the photoconductors of the present invention can include a wide variety of organic solvents for the components of the coating composition. For example, benzene; toluene; acetone; 2-butanone; chlorinated hydrocarbons such as methylene chloride; ethylene chloride; and the like; ethers, such as tetrahydrofuran and the like, or mixtures of such solvents can advantageously be employed in the practice of this invention.

In preparing the coating compositions utilizing the photoconductors disclosed herein useful results are obtained where the photoconductive substance is present in an amount equal to at least about 1 weight percent of the coating composition. The upper limit in the amount of photoconductive material present can be widely varied in accordance with usual practice. It is normally required that the photoconductive material be present in an amount ranging from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductive material in the coating composition is from about 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally, a wet coating thickness in the range of about 0.001 inch to about 0.01 inch is useful in the practice of the invention. A preferred range of coating thickness is from about 0.002 inch to about 0.006 inch before drying although such thicknesses can vary widely depending on the particular application desired for the electrophotographic element.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of the 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 or aluminum on conventional film supports such as cellulose acetate, poly(ethylene terephthalate), polystyrene and the like conducting supports.

An especially useful conducting support can be prepared by coating a transparent film support material such as poly(ethylene terephthalate) with a layer containing a semiconductor dispersed in a resin. A suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone of the maleic anhydride-vinyl acetate copolymer, cuprous iodide and the like. Such conducting layers and methods for their optimum preparation and use are disclosed in U.S. Pat. Nos. 3,007,901, 3,245,833 and 3,267,807.

The compositions of the present invention can be employed in photoconductive elements useful in any of the wellknown electrophotographic processes which require photoconductive layers. One such process is the xerographic process. In a process of this type, an electrophotographic element held in the dark, is given a blanket electrostatic charge by placing it under a corona discharge to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer owing to the substantial dark insulating property of the layer, i.e., the lower 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, or reflex or bireflex techniques 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, or powder and generally comprise a pigment in a resinous carrier called a toner. A preferred method of applying such a 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; 2,786,440; 2,786,441; 2,811,465; 2,874,063; 2,984,163; 3,040,704; 3,117,884; and reissue Re 25,779. 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. 2,297,691 and in Australian Pat. No. 212,315. 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 charge image or powder image formed on the photoconductive layer can be made to a second support such as paper which would then become the final print after developing and fusing or fusing respectively. Techniques of the type indicated are well known in the art and have been described in a number of U.S. and foreign patents, such as U.S. Pat. Nos. 2,297,691 and 2,551,582, and in "RCA Review," vol. 15 (1954) pages 469–484.

The compositions of the present invention can be used in electrophotographic elements having many structural variations. For example, the photoconductive composition can be coated in the form of single layers or multiple layers on a suitable opaque or transparent conducting support. Likewise, the layers can be contiguous or spaced having layers of insulating material or other photoconductive material between layers or overcoated or interposed between the photoconductive layer or sensitizing layer and the conducting layer. It is also possible to adjust the position of the support and the conducting layer by placing a photoconductor layer over a support and coating the exposed face of the support or the exposed or overcoated face of the photoconductor with a conducting layer. Configurations differing from those contained in the examples can be useful or even preferred for the same or different application for the electrophotographic element.

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

Example 1

A composition in the form of a dope consisting of
Organic photoconductor—.31 g
Polymeric binder(Lexan 105, a polycarbonate resin sold by General Electric Co.)—.94 g
Sensitizer(2,4-bis(4-ethoxyphenyl)-6-(4-amyloxystyryl) pyrylium fluoroborate—.0125 g
Methylene chloride—10.00 g

is coated at a wet thickness of 0.004 inch on an aluminum surface to provide the coatings described in Table II. In a darkened room, the surface of the photoconductive layer, so prepared, is charged to a potential of about +600 volts under a corona charger. The layer is then covered with a transparent sheet bearing a pattern of opaque and light-transmitting areas and exposed to the radiation from an incandescent lamp with an illumination intensity of about 75 meter-candles for 12 seconds. The resulting electrostatic latent image is developed by cascading over the surface of the layer a mixture of negatively charged thermoplastic toner particles and glass beads. A good reproduction is obtained in each instance.

TABLE II

	Photoconductor	Image Reproduced
	None present	No
I	N,N-Dibenzylaniline	Yes
II	N-Benzyl-N-phenylaniline	Yes
III	N,N-Bis(cyclohexylmethyl) aniline	Yes
IV	N,N-Bis(cyclohexylethyl) aniline	Yes

Example 2

Coatings containing 25% of an N,N-dialkylaniline in Lexan 105 and sensitized with 1% 2,4-bis(4-ethylphenyl)-6-(4-styrylstyyl)pyrylium perchlorate are prepared and examined by the procedure in Example 1. The results are listed in Table III.

TABLE III

	Photoconductor	Image Reproduced
I	N,N-Dibenzylaniline	Yes
II	N,N-Diphenethylaniline	Yes
III	N,N-Bis(cyclohexylmethyl) aniline	Yes
IV	N,N-Bis(cyclohexylethyl) aniline	Yes
	None present	No

Example 3

Coatings containing 20% of N,N-diethylaniline (VI) in Lexan 105 and sensitized with 1% 2,4-bis(4-ethylphenyl)-6-(4-styrylstyryl)pyrylium perchlorate are prepared and examined according to the procedure described in Example 1. The coatings are charged to about +620 volts and on exposure and development a good image is obtained. Similarly good reproductions are obtained when 1-dimethylaminonaphthalene (VII) or 1-diethylaminonaphthalene (VIII) are used instead of diethylaniline. When the aniline derivative is omitted, no image is obtained.

Example 4

Coatings containing 23% of N-ethyl-N-phenylaniline (IX) photoconductor in Vitel 101 polyester with 0.3% 2,4,7-trinitrofluorenone sensitizer are prepared by the method in Example 1 from a dope consisting of

0.15 g—Photoconductor
0.50 g—Vitel 101— a polyester resin sold by Goodyear Tire & Rubber Co. comprising essentially poly)4,4'-isopropylidenebisphenoxyethyl-co-ethylene terephthalate)
0.002 g—Sensitizer
5 ml—Dichloromethane

and examined according to the procedure set forth in Example 1. A good reproduction is obtained. When the photoconductor is omitted, no image is reproduced.

Example 5

Coatings containing 25% of N-ethyl-N-4-n-octylphenyl-4'-n-octylaniline (X) in polystyrene binder with 1% of 2,6-bis(4-ethylphenyl)-6-(4-pentyloxyphenyl)-thiapyrylium perchlorate sensitizer are prepared as described in Example 1 and the speeds are measured by exposure through a 0.15 log E step wedge and development of the resulting latent image with a positive fringe toner. The number of visible steps developed is 14. When the aniline compound is omitted, no complete visible steps are obtained.

Example 6

Coatings containing 25% of N,N'-diethyl-N,N'-diphenylethylenediamine (XI) in Vitel 101 binder with 1% 2,6-bis(4-ethylphenyl)-6-(4-pentyloxyphenyl)-thiapyrylium perchlorate sensitizer are prepared and evaluated as described in Example 5. The number of visible steps developed is 18, when the aniline is omitted only ten visible steps are reproduced.

Example 7

Coatings containing 20% of N-cyclohexyl-N-phenylaniline (XII) photoconductor in Vitel 101 polyester with 0.8% 2,6-bis(4-ethylphenyl)-4-(4-pentyloxyphenyl)thiapyrylium perchlorate are prepared and tested by the method in Example 1 from a dope consisting of

0.25 g—Photoconductor
1.00 g—Vitel 101
0.01 g—Sensitizer
9.6 g— Dichloromethane

A good reproduction of the original is obtained for both positive and negative charging.

Example 8

Example 7 is repeated except that the photoconductor employed is N-styryl-N-phenylaniline (XVII). Again, a good reproduction is obtained.

Example 9

Coatings containing 20% of aniline derivatives N-ethyl-N-phenylaniline (IX) or N-ethyl-N-(2-phenoxyethyl)-3-methylaniline in Lexan 105 and sensitized with 1% 2,6-bis(4-ethoxyphenyl)-4-(4-pentyloxyphenyl)thiapyrylium perchlorate are prepared and examined by the procedure in Example 1. The results are listed in Table IV.

TABLE IV

20% Photoconductor in Lexan 105 with 1% Sensitizer

		Image Reproduced
IX	N-Ethyl-N-phenylaniline	Yes
XIV	N-Ethyl-n-(2-phenoxyethyl)-3-methylaniline	Yes
	None present	No

Example 10

Several compositions are prepared comprising Vitel 101 polyester binder, 20% by weight photoconductor and 0.8% by weight of the sensitizer 2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate all dissolved in methylene chloride. The resultant dopes are coated as in Example 1 to form elements 1 through 6 each of which is charged under a negative corona and imagewise exposed to a 3,000° K tungsten source through a neutral 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_o, to some lower potential, V, whose exact value depends upon the actual amount of exposure in meter-candle-seconds received by the area. The results of these measurements are then plotted on a graph of surface potential V vs. log exposure for each step. The actual 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. Herein, unless otherwise stated, the actual negative speed is the numerical expression of 104 divided by the exposure in meter-candle-seconds required to reduce the initially charged surface potential V_o to a value 100 volts lower (shoulder speed) and to an absolute value of 100 volts (toe speed). In addition, the contrast is determined as the tangent of the angle made by extending the straight line portion of the electrical speed curve in mid-scale to the base axis. The results of these measurements using different photoconductors of the prior art (elements 2 through 6) are shown below.

Element No.	Photoconductor	Speed Shoulder/Toe	Contrast
1	N,N-Dibenzylaniline	220/3.0	1.04
2	Di-2-naphthylamine	50/0	1.23
3	N-Phenyl-2-naphthylam8ne	36/0	1.04
4	N-Phenyl-1-naphthylamine	32/0	1.07
5	Diphenylamine	*	*
6	2,5-Bis(p-diethylamino phenyl)-1,3,4-oxadiazole	63/4.0	1.66

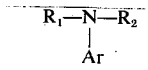
*Speed too low to obtain a meaningful sensitometric curve.

The above indicates the low contrast and good speed obtained with a photoconductor of the present invention. Whereas, prior conductors have low or no speed and/or high contrast.

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

I claim:

1. A photoconductive composition comprising a polymeric film-forming binder, an organic photoconductor and a sensitizing amount of a sensitizer for said photoconductor, said photoconductor having the formula:



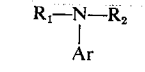
wherein:

R_1 is selected from the group consisting of an alkyl group having up to 18 carbon atoms, a phenyl group, a naphthyl group, an anthryl group, a fluorenyl group and a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus;

R_2 is selected from the group consisting of an alkyl group having up to 18 carbon atoms and a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus; and

Ar is selected from the group consisting of phenyl, naphthyl,anthryl and fluorenyl.

2. An electrophotographic element comprising a conductive support having thereon a photoconductive composition comprising a polymeric film-forming binder, an organic photoconductor and a sensitizing amount of a sensitizer for the photoconductor, said photoconductor having the formula:



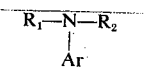
wherein:

R_1 is selected from the group consisting of an alkyl group having up to 18 carbon atoms, a phenyl group, a naphthyl group, an anthryl group, a fluorenyl group and a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus;

R_2 is selected from the group consisting of an alkyl group having up to 18 carbon atoms and a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus; and

Ar is selected from the group consisting of phenyl, naphthyl, anthryl and fluorenyl.

3. In an electrophotographic process for forming low contrast images wherein an electrostatic charge pattern is formed on an electrophotographic element which comprises a conductive support having thereon a photoconductive layer comprising a polymeric film-forming binder, an organic photoconductor and a sensitizer for said photoconductor, the improvement wherein said photoconductor has the formula:



wherein:

R_1 is selected from the group consisting of an alkyl group having up to 18 carbon atoms, a phenyl group, a naphthyl group, an anthryl group, a fluorenyl group and a cycloalkyl group having four to eight carbon atoms in the cyclic nucleus;

R_2 is selected from the group consisting of an alkyl group having up to 18 carbon atoms and a cycloal-

kyl group having four to eight carbon atoms in the cyclic nucleus; and

Ar is selected from the group consisting of phenyl, naphthyl, anthryl and fluorenyl.

4. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising

a. from about 10 to about 60 percent by weight based on said photoconductive composition of N,N-dibenzylaniline as a photoconductor,

b. a film-forming polymeric binder for said photoconductor and

c. 0.005% to about 5% by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

5. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising

a. from about 10 to about 60 percent by weight based on said photoconductive composition of N-benzyl-N-phenylaniline as a photoconductor,

b. a film-forming polymeric binder for said photoconductor and

c. 0.005% to about 5% by weight based on said photoconductive composition of a sensitizer for said photo-conductive composition.

6. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising

a. from about 10 to about 60 percent by weight based on said photoconductive composition of N,N-bis(cyclohexylmethyl)aniline as a photoconductor,

b. a film-forming polymeric binder for said photoconductor and

c. 0.005% to about 5% by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

7. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising

a. from about 10 to about 60 percent by weight based on said photoconductive composition of N,N-bis(cyclohexylethyl)aniline as a photoconductor,

b. a film-forming polymeric binder for said photoconductor and

c. 0.005% to about 5% by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

8. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising

a. from about 10 to about 60 percent by weight based on said photoconductive composition of N,N-diphenethylaniline as a photoconductor,

b. a film-forming polymeric binder for said photoconductor and

c. 0.005% to about 5% by weight based on said photoconductive composition of a sensitizer for said photoconductive composition.

* * * * *