

[54] 1-AMINOPYRIDINIUM DYES AS SENSITIZERS IN ELECTROPHOTOGRAPHIC LAYERS

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[58] Field of Search .....96/1.6, 1.7, 102, 140; 260/240, 240.4

[56] References Cited

UNITED STATES PATENTS

2,839,403 6/1958 Knott .....260/240.4 X

Table with 3 columns: Patent Number, Date, and Inventor/Reference. Includes entries for Greig, Davis, Van Allan et al., Seidel et al., Menold et al., Fox et al., and Murakami et al.

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[57] ABSTRACT

1-Aminopyridinium dyes are useful for sensitizing photoconductive compositions used in electrophotographic layers. The dyes are heat and light bleachable so that undesirable color imparted to background areas of the image bearing element by the dyes is easily removable. Such bleaching increases the visual contrast of the reproduction.

10 Claims, No Drawings

# 1-AMINOPYRIDINIUM DYES AS SENSITIZERS IN ELECTROPHOTOGRAPHIC LAYERS

This invention relates to electrophotography, and in particular to novel sensitized photoconductive compositions and elements having coated thereon such compositions.

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 actinic 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 the surface charge in accordance with the relative energy contained in various parts of the radiation pattern. The differential surface charge or electrostatic charge 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 the absence of charge pattern as desired. The deposited marking material may then be either permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor, or the like, or transferred to a second element to which it may similarly be fixed. Likewise, the electrostatic charge image can be transferred to a second element and developed there.

Various photoconductive insulating materials have been 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 present-day document 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 are known to possess some degree of photoconductivity. Many organic compounds have revealed a useful level of photoconduction and have been incorporated into photoconductive compositions. Optically clear organic photoconductor-containing elements having desirable electrophotographic properties can be especially useful in electrophotography. Such electrophotographic elements may be exposed through a transparent base if desired, thereby providing unusual flexibility in equipment design. Such compositions, when coated as a film or layer on a suitable support also yield an element which is reusable; that is, it can be used to form subsequent images after residual toner from prior images has been removed by transfer and/or cleaning.

Although some of the organic photoconductors comprising the materials described are inherently light sensitive, their degree of sensitivity is usually low and in the short wave-length portion of the spectrum so that it is common practice to add materials to increase the speed and to shift the sensitivity toward the longer wave-length portion of the visible spectrum. Increasing the speed and shifting the sensitivity of such systems into the visible region of the spectrum has several advantages: it makes available inexpensive and convenient light sources such as incandescent lamps; it reduces exposure time; it makes possible the recording of a wide range of colors in proper tonal relationship, and allows projection printing through various optical systems. By increasing the speed through the use of sensitizers, photoconductors which would otherwise have been unsatisfactory are useful in processes where high speeds are required such as document copying.

A primary disadvantage associated with the use of sensitizers is that, because they are usually highly colored, they may impart undesirable discoloration to the entire photoconductive element. As a result, an image developed directly on

the surface of the element can be viewed only with great difficulty because of the low visual contrast between toned and untoned areas. Furthermore, such an element bearing a developed image is generally unsuitable for use as a master for the making of further reproductions.

It is therefore an object of this invention to provide novel sensitized photoconductive elements.

It is another object of this invention to provide novel sensitized photoconductive compositions.

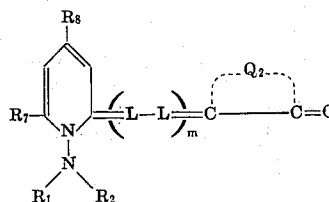
It is a further object of this invention to provide a process for bleaching the novel sensitized photoconductive elements.

These and other objects are accomplished with photoconductive compositions containing a photoconductor and a 1-aminopyridinium dye as a sensitizer for the photoconductive composition. According to this invention, it has been found that when 1-aminopyridinium dyes are used in photoconductive compositions, an enhanced sensitization effect is realized. Photoconductive compositions which do not contain the sensitizers of this invention frequently do not produce good quality images when used in element form in an electrophotographic process.

An advantage resulting from the employment of the 1-aminopyridinium sensitizers herein in photoconductive compositions is that good quality images are obtainable when the compositions are coated on supports and used in electrophotographic processes. Another advantage is that the intensity of the color imparted to the coated compositions by the sensitizers can be substantially reduced i.e., bleached, by subjecting the elements to actinic radiation, e.g., a light exposure of at least  $6 \times 10^4$  foot-candle-seconds. Also, elements containing the sensitizers of this invention can be bleached by heating to a temperature of at least about  $140^\circ \text{C}$ . for at least about 15 seconds. Generally, there is no practical advantage in using exposures of greater than  $10^8$  foot-candle-seconds or heating to temperatures in excess of  $250^\circ \text{C}$ . for more than 1 hour. Bleaching can be accelerated by combining heat with light exposure. The most rapid bleaching is obtained by using the above heating conditions while simultaneously exposing the element to light giving an illuminance of at least 4,000 foot-candles. Sources combining ultraviolet with visible light are particularly effective, e.g. tungsten-halogen lamps.

The fact that the sensitizers used in the element can be bleached is significant from the standpoint of being able to view an image which is developed directly on the surface of the electrophotographic element and also being able to use the visible-image-bearing element as a master from which further prints can be made on a wide variety of materials. Bleaching causes substantial reduction of the optical opacity in the background areas, thus permitting the uses described above. In order to obtain these advantages using many other known sensitizers which are highly colored, the electrostatic charge image must be transferred to a receiving element and developed there or, if developed on the surface of the electrophotographic element, the visible image must be transferred to a receiving sheet before it can be viewed.

The preferred 1-aminopyridinium sensitizing dyes of this invention have the following formula:



wherein

R<sub>1</sub> and R<sub>2</sub> when taken separately can be

a. an alkyl group preferably having one to eight carbon atoms such as methyl, ethyl, propyl, butyl, etc. including a substituted alkyl radical such as aralkyl, e.g., benzyl; hydroxyalkyl such as hydroxypropyl, hydroxyethyl, etc.;

b. an acyl group; e.g.,

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including a thiaacyl group, e.g.,



wherein  $\text{R}_3$  is an alkyl group preferably having one to eight carbon atoms such as methyl, ethyl, propyl, butyl, etc., an aryl group such as phenyl, naphthyl, tolyl, etc., an alkoxy group containing one to eight carbon atoms such as methoxy, ethoxy, butoxy, isobutoxy, etc., an amino group such as arylamino, alkylamino, etc., a heterocyclic nucleus containing five to six members at least one of which is oxygen, sulfur or nitrogen such as a pyridine nucleus, a quinoline nucleus, etc.;

c. hydrogen;

d. an aryl radical including a substituted aryl radical, e.g., phenyl, naphthyl, tolyl, hydroxyphenyl, halophenyl such as chlorophenyl, 2,4,6-trichlorophenyl, nitrophenyl, carboxyphenyl, alkoxyphenyl such as methoxyphenyl, ethoxyphenyl, etc.,

e. a heterocyclic nucleus containing five to six members in the nucleus at least one member being a nitrogen, sulfur, selenium or oxygen atom including a substituted heterocyclic nucleus, such as a pyridine nucleus, a quinoline nucleus, a benzothiazole nucleus, etc.;

f. when taken together represent the atoms necessary to complete a five to six membered heterocyclic nucleus including a substituted heterocyclic nucleus such as a 4H-1,2,4-triazolyl, an alkyl substituted 4H-1,2,4-triazolyl, an aryl substituted 4H-1,2,4-triazolyl, a morpholino group, an imidazole group, a piperidino group, a pyrrole group, a pyrrolidino group, etc.;

$\text{Q}_2$  represents the non-metallic atoms required to complete a five to six membered heterocyclic nucleus, typically containing a hetero atom selected from nitrogen, sulfur, selenium, and oxygen, such as a 2-pyrazoline-5-one nucleus (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.); an isoxazolone nucleus (e.g., 3-phenyl-5-(4H)-isoxazolone, 3-methyl-5-(4H)-isoxazolone, 3-methyl-5-(4H)-isoxazolone, etc.); an oxindole nucleus (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl, 1-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di( $\alpha$ -methoxyethyl), etc.) or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc. or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives), a rhodanine nucleus (e.g., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines (e.g., 3-ethylrhodanine, 3-allylrhodanine, etc.), 3-carboxyalkylrhodanines (e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc.), 3-sulfoalkyl rhodanines (e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl) rhodanine, 3-(4-sulfobutyl)rhodanine, etc.), or 3-arylrhodanines (e.g., 3-phenylrhodanine, etc.), etc.; a 2(3H)-imidazo[1,2-a]-pyridone nucleus; a 2-furanone nucleus (e.g., 3-cyano-4-phenyl-2(5H)-furanone); a thiophen-3-one-1,1-dioxide nucleus (e.g., benzo[b]thiophen-3(2H)-one-1,1-dioxide); a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]-pyrimidine nucleus (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.); a pyrrolo[1,2-a]pyrimidine-2,4(3H)-dione nucleus; a 2-thio-2,4-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4-(3H,5H)-oxazolidinedione series) (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione, etc.); a thianaphthenone nucleus (e.g., 2-(2H)-thianaphthenone, etc.); a 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5(3

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H,4H)-thiazolidinedione series) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.); a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3- $\alpha$ -naphthyl-2,4-thiazolidinedione, etc.); a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3- $\alpha$ -naphthyl-4-thiazolidinone, etc.); a 2-thiazolin-4-one series (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkyl-phenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.); a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus; a 2,4-imidazolidinedione (hydantoin) series (e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3- $\alpha$ -naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidinedione, 1-ethyl-2- $\alpha$ -naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.); a 2-thio-2,4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3- $\alpha$ -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3- $\alpha$ -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.); a 2-imidazolin-5-one nucleus (e.g., 2-propylthio-2-imidazolin-5-one, etc.);

$m$  is a positive integer from 1 to 2;

L represents a methine linkage having the formula



wherein T can be hydrogen, lower alkyl of one to four carbon atoms or aryl, such as phenyl, e.g.,  $-\text{CH}=\text{C}(\text{C}_6\text{H}_5)=$ , etc.;

$\text{R}_7$  and  $\text{R}_8$  each can be (1) a hydrogen atom, (2) an alkyl group (preferably a lower alkyl containing from one to four carbon atoms) including a substituted alkyl group such as aralkyl, hydroxyalkyl, e.g., methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, dodecyl, benzyl, hydroxypropyl, hydroxyethyl, etc. or (3) an aryl group including a substituted aryl group such as an alkaryl, haloaryl, alkoxyaryl, aminoaryl, etc. e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, diethylaminophenyl, etc.;

Typical compounds which belong to the herein described general class of sensitizing dyes include the following:

- I 3-[(1-N-methylanilino-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- II 3-[(1-diethylamino-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- III 3-[1-amino-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- IV 3-[(1-{N-methyl-N-4-pyridylamine}-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- V 3-[(1-acetanilido-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- VI 3-[(1-pyridyl-4,6-di-p-tolyl-2(1H)-pyridylidene)ethylidene]2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- VII 3-[(1-N-methylanilino-4-p-tolyl-2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- VIII 3-[(1-diethylamino-4-p-tolyl-2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione
- IX 3-[(1-amino-4-p-tolyl-2(1H)-pyridylidene)ethylidene]2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione

X 3-[(1-[N-methyl-N-4-pyridylamine]-4-p-tolyl-b  
2(1H)-pyridylidene)ethylidene]-2H-pyrido[1,2-a  
]pyrimidine-2,4(3H)-dione

XI 3-[(1-acetanilido-4-p-tolyl-2(1H)-pyridy-  
lidene)ethylidene]2H-pyrido[1,2-a]pyrimidine-2,4(3H)-  
dione

XII 3-[(1-pyridyl-4-p-tolyl-2(1H)-pyridylidene)ethy-  
lidene]2H-pyrido[1,2-a]pyrimidine-2,4(3H)-dione

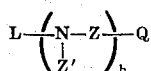
Electrophotographic elements of the invention can be prepared with any photoconductive compound and the sensitizers of this invention in the usual manner, i.e., by blending a dispersion or solution of the photoconductive compound together with a binder, when necessary or desirable, and coating or forming a self-supporting layer with the photoconductive composition. Generally, a suitable amount of the sensitizing compound is mixed with the photoconductive coating composition so that, after thorough mixing, the sensitizing compound is uniformly distributed throughout the desired layer of the coated element. The amount of sensitizer that can be added to a photoconductor-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 of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount from about 0.005 to about 5.0 percent by weight of the total coating composition.

The sensitizers of this invention improve the electrical speeds of compositions containing a wide variety of photoconductors including inorganic photoconductors such as zinc oxide, titanium dioxide, cadmium sulfide and the like, organic photoconductors including organometallic photoconductors and mixtures thereof.

Typical additional photoconductors useful with the binders of this invention are described below.

A. Arylamine photoconductors including substituted and unsubstituted arylamines, diarylamines, nonpolymeric triarylamines and polymeric triarylamines such as those described in U.S. Pat. Nos. 3,240,597 and 3,180,730.

B. Photoconductors represented by the formula



wherein Z represents a mononuclear or polynuclear divalent aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, binaphthyl, etc.), or a substituted divalent aromatic radical of these types wherein said substituent can comprise a member such as an acyl group having from one to about six carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from one to about six carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from one to about six carbon atoms (e.g., methoxy, ethoxy, propoxy, pentoxy, etc.), or a nitro group; Z' represents a mononuclear or polynuclear monovalent or polynuclear monovalent aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.); or a substituted monovalent aromatic radical wherein said substituent can comprise a member, such as an acyl group having from one to about six carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from one to about six carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from one to about six carbon atoms (e.g., methoxy, propoxy, pentoxy, etc.), or a nitro group; Q can represent a hydrogen atom or an aromatic amino group, such as Z'NH—; b represents an integer from 1 to about 12, and L represents a hydrogen atom, a mononuclear or polynuclear aromatic radical, either fused or linear (e.g., phenyl, naphthyl, biphenyl, etc.), a substituted aromatic radical wherein said substituent comprises an alkyl group, an alkoxy group, an acyl group, or a nitro group, or a poly(4'-vinylphenyl) group which is bonded

to the nitrogen atom by a carbon atom of the phenyl group, these materials being more fully described in U.S. Pat. No. 3,265,496.

C. Polyaryllkane photoconductors including leuco bases of diaryl or triarylmethane dye salts, 1,1,1-triaryllkanes wherein the alkane moiety has at least two carbon atoms and tetraaryllkanes having an amino group substituted in at least one of the aryl nuclei attached to the alkane and methane moieties of the latter two classes of photoconductors which are non-leuco base materials; and also other polyaryllkanes included by the formula:

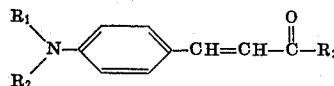


wherein each of D, E and G is an aryl group and J is a hydrogen atom, an alkyl group, or an aryl group, at least one of D, E and G containing an amino substituent, the aryl groups attached to the central carbon atom being preferably phenyl groups, although naphthyl groups can also be used including substituted aryl groups containing substituents such as alkyl and alkoxy typically having one to eight carbon atoms, hydroxy, halogen, etc., in the ortho, meta or para positions, ortho-substituted phenyl being preferred; the aryl groups can also be joined together or cyclized to form a fluorene moiety, for example; the amino substituent can be represented by the formula

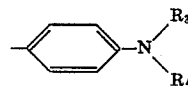


wherein each R can be an alkyl group typically having one to eight carbon atoms, a hydrogen atom, an aryl group, or together the necessary atoms to form a heterocyclic amino group typically having five to six atoms in the ring such as morpholino, pyridyl, pyrrol, etc.; at least one of D, E and G preferably being a p-dialkylaminophenyl group, when J is an alkyl group, such an alkyl group more generally has one to seven carbon atoms, these materials being more fully described in U.S. Pat. No. 3,274,000, French Pat. No. 1,383,461 and in U.S. Ser. No. 627,857 filed Apr. 3, 1967 by Seus and Goldman.

D. Photoconductors comprising 4-diarylamino substituted chalcones having the formula:



wherein R<sub>1</sub> and R<sub>2</sub> are each phenyl radicals including substituted phenyl radicals, R<sub>2</sub> preferably having the formula:

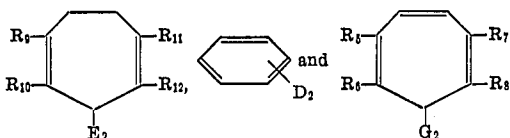


wherein R<sub>3</sub> and R<sub>4</sub> are each aryl radicals, aliphatic residues of one to 12 carbon atoms such as alkyl radicals preferably having one to four carbon atoms, or hydrogen; particularly advantageous results being obtained when R<sub>1</sub> is a phenyl radical including a substituted phenyl radical and where R<sub>2</sub> is diphenylaminophenyl, dimethylaminophenyl or phenyl, these materials being more fully described in Fox application U.S. Ser. No. 613,846, filed Feb. 3, 1967, now U.S. Pat. No. 3,526,501.

E. Non-ionic cycloheptenyl compounds which may be substituted with substituents such as:

1. an aryl radical including substituted as well as unsubstituted aryl radicals,
2. a hydroxy radical,
3. an azido radical,
4. a heterocyclic radical having five to six atoms in the heterocyclic nucleus and at least one hetero nitrogen atom, and including substituted and unsubstituted heterocyclic radicals, and
5. an oxygen linked cycloheptenyl moiety.

The substitution on the cycloheptenyl nucleus occurs at an unsaturated carbon atom when the cycloheptenyl moiety is a conjugated triene with no aromatic structure fused thereto. However, if there is at least one aromatic structure fused to the cycloheptenyl moiety, then the substituents are attached to a saturated carbon atom. Additional photoconductors within this class are included in one of the following formulae:



where  $E_2$  and  $G_2$  can be either:

1. a phenyl radical,
2. a naphthyl radical,
3. a heterocyclic radical having five to six atoms in the heterocyclic nucleus and at least one hetero nitrogen atom,
4. a hydroxyl radical, or
5. an oxygen containing radical having a structure such that the resultant cycloheptenyl compound is a symmetrical ether;

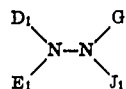
$D_2$  can be any of the substituents defined for  $E_2$  and  $G_2$  above and is attached to a carbon atom in the cycloheptenyl nucleus having a double bond; ( $R_9$  and  $R_{10}$ ), ( $R_{11}$  and  $R_{12}$ ), ( $R_5$  and  $R_6$ ), and ( $R_7$  and  $R_8$ ) are together the necessary atoms to complete a benzene ring fused to the cycloheptenyl nucleus; these compounds being more fully described in U.S. Ser. No. 654,091 filed July 18, 1967, now U.S. Pat. No. 3,533,786.

F. Compounds containing an



nucleus including:

1. unsubstituted and substituted N, N-bicarbazyls containing substituents in either or both carbazolyl nuclei such as:
  - a. an alkyl radical including a substituted alkyl radical such as a haloalkyl or an alkoxyalkyl radical,
  - b. a phenyl radical including a substituted phenyl radical such as a naphthyl, an aminophenyl or a hydroxyphenyl radical,
  - c. a halogen atom,
  - d. an amino radical including substituted as well as unsubstituted amino radicals such as an alkylamino or a phenylalkylamino radical,
  - e. an alkoxy radical,
  - f. a hydroxyl radical,
  - g. a cyano radical,
  - h. a heterocyclic radical such as a pyrazolyl, carbazolyl or a pyridyl radical; or
2. tetra-substituted hydrazines containing substituents which are substituted or unsubstituted phenyl radicals, or heterocyclic radicals having five to six atoms in the hetero nucleus, suitable results being obtained when all four substituents are not unsubstituted phenyl radicals, i.e., if at least one substituent is a substituted phenyl radical or a heterocyclic radical having five to six atoms in the hetero nucleus. Other tetra-substituted hydrazines include those having the following formula:

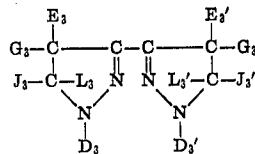


wherein  $D_1$ ,  $E_1$ ,  $G_1$  and  $J_1$  are each either:

- a. a substituted phenyl radical such as a naphthyl radical, an alkyl phenyl radical, a halophenyl radical, a hydroxyphenyl radical, a haloalkylphenyl radical or a hydroxyalkylphenyl radical, or
- b. a heterocyclic radical such as an imidazolyl radical, a furyl radical, or a pyrazolyl radical. In addition  $J_1$  and  $E_1$  can also be
- c. an unsubstituted phenyl radical.

Especially preferred are those tetra-substituted hydrazines wherein both  $D_1$  and  $G_1$  are either substituted phenyl radicals or heterocyclic radicals. These compounds are more fully described in U.S. Ser. No. 673,962 filed Oct. 9, 1967.

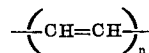
G. Organic compounds having a 3,3'-bis-aryl-L-2-pyrazoline nucleus which is substituted in either five-member ring with the same or different substituents. The 1 and 5 positions on both pyrazoline rings can be substituted by an aryl moiety including unsubstituted as well as substituted aryl substituents such as alkoxyaryl, alkaryl, alkaminoaryl, carboxyaryl, hydroxyaryl and haloaryl. The 4 position can contain hydrogen or unsubstituted as well as substituted alkyl and aryl radicals such as alkoxyaryl, alkaryl, alkaminoaryl, haloaryl, hydroxyaryl, alkoxyalkyl, aminoalkyl, carboxyaryl, hydroxyalkyl and haloalkyl. Other photoconductors in this class are represented by the following structure:



wherein:

$D_3$ ,  $D_3'$ ,  $J_3$  and  $J_3'$  can be either a phenyl radical including a substituted phenyl radical such as a tolyl radical or a naphthyl radical including a substituted naphthyl radical,  $E_3$ ,  $E_3'$ ,  $G_3$ ,  $G_3'$ ,  $L_3$  and  $L_3'$  can be any of the substituents set forth above and in addition can be either a hydrogen atom or an alkyl radical containing one to eight carbon atoms. These organic photoconductors are more fully described in U.S. Ser. No. 664,642 filed Aug. 31, 1967, now U.S. Pat. No. 3,527,602.

H. Triarylamines in which at least one of the aryl radicals is substituted by either a vinyl radical or a vinylene radical having at least one active hydrogen-containing group. The phrase "vinylene radical" includes substituted as well as unsubstituted vinylene radicals and also includes those radicals having at least one and as many as three repeating units of vinylene groups such as



wherein  $n$  is an integer of from 1 to 3. Groups which contain active hydrogen are well known in the art, the definition of this term being set forth in several textbooks such as "Advanced Organic Chemistry," R. C. Fuson, pp. 154-157, John Wiley & Sons, 1950. The term "active hydrogen-containing group" as used herein includes those compounds encompassed by the discussion in the textbook cited above and in addition includes those compounds which contain groups which are hydrolyzable to active hydrogen-containing groups. Typical active hydrogen-containing groups substituted on the vinylene radical of the triarylamine include:

1. carboxy radicals,
2. hydroxy radicals,
3. ethynyl radicals,
4. ester radicals (e.g.,



wherein  $R_{13}$  is alkyl or aryl) including cyclic ester radicals (e.g.,



wherein  $R_{14}$  is a cyclic alkylene radical connected to a vinylene combination such as is found in coumarin derivatives),

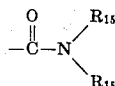
5. carboxylic acid anhydride radicals,
6. semicarbazono radicals,
7. cyano radicals,

8. acryl halide radicals (e.g.,



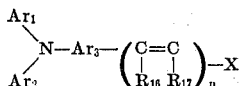
etc.), and

9. amido radicals (e.g.,



wherein  $R_{15}$  is a hydrogen atom, an alkyl group or an aryl group).

Other active hydrogen-containing groups include substituted and unsubstituted alkylidyne oximido radicals. Photoconductors included in this class can be represented by the following structure:



wherein:

1.  $\text{Ar}_1$  and  $\text{Ar}_2$  are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an aminophenyl radical,
2.  $\text{Ar}_3$  is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical,
3.  $\text{R}_{16}$  and  $\text{R}_{17}$  are each hydrogen, a phenyl radical including a substituted phenyl radical or a lower alkyl radical preferably having one to eight carbon atoms,
4. X is either:
  - a. an active hydrogen-containing group such as a carboxy radical, an acyl halide radical, an amido radical, a carboxylic acid anhydride radical, an ester radical, a cyano radical, a hydroxy radical, a semicarbazono radical, an ethynyl radical, or a methylidyne oximido radical or
  - b. hydrogen provided that when X is hydrogen  $\text{R}_{16}$  and  $\text{R}_{17}$  are also hydrogen, and
5.  $n$  is an integer of 1 to 3.

The arylene nucleus can be substituted in any position by the vinyl or vinylene moiety. However, when  $\text{Ar}_3$  is phenylene, particularly good results are obtained if the substitution occurs in the para position. These materials are more fully described in U.S. Ser. No. 706,800 filed Feb. 20, 1968, now U.S. Pat. 3,567,450.

I. Triarylamines in which at least one of the aryl radicals is substituted by an active hydrogen-containing group. The term "active hydrogen-containing group" has the same meaning as set forth above and again includes those compounds encompassed by the discussion in the textbook and additionally includes those compounds which contain groups which are hydrolyzable to active hydrogen-containing groups. Typical active hydrogen-containing groups which are substituted on an aryl radical of the triarylamine include:

1. carboxy radicals,
2. hydroxy radicals,
3. ethynyl radicals,
4. ester radicals (e.g.,



wherein  $R_{18}$  is an alkyl or an aryl group),

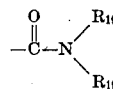
5. lower alkylene hydroxy radicals (e.g., having one to eight carbon atoms,
6. carboxylic acid anhydride radicals,
7. lower alkylene carboxy radicals (e.g., having two to eight carbon atoms),
8. cyano radicals,

9. acryl halide radicals (e.g.,



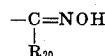
etc.),

10. amido radicals (e.g.,



wherein  $R_{19}$  is a hydrogen atom, an alkyl group or an aryl group),

- 20 11. lower alkylidyne oximido radicals having one to eight carbon atoms including substituted alkylidyne oximido radicals (e.g.,



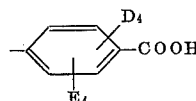
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wherein  $R_{20}$  is hydrogen or a lower alkyl radical),

12. semicarbazono radicals, and

13. arylene carboxy radicals including substituted arylene carboxy radicals (e.g.,

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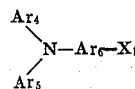


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wherein  $D_4$  and  $E_4$  are phenyl or lower alkyl radicals.

Photoconductors included in this class can be represented by the following structure:

40



wherein:

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- a.  $\text{Ar}_1$  and  $\text{Ar}_2$  are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an amino phenyl radical,
- b.  $\text{Ar}_6$  is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical, and
- c.  $\text{X}_1$  is an active hydrogen-containing group such as a carboxy radical, an acyl halide radical, an amido radical, a carboxylic acid anhydride radical, an ester radical, a cyano radical, a semicarbazono radical, a hydroxy radical, an ethynyl radical, a methylidyne oximido radical or a phenylene carboxy radical.

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These materials are more fully described in U.S. Ser. No. 706,780 filed Feb. 20, 1968, now U.S. Pat. No. 3,567,450.

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J. Organo-metallic compounds having at least one amino-aryl substituent attached to a Group IVa or Group Va metal atom. The metallic substituents of this class of organic photoconductors are Group IV or Group Va metals in accordance with the Periodic Table of the Elements (Handbook of Chemistry and Physics, 38th edition, pp. 394-95) and include silicon, germanium, tin and lead from Group IVa and phosphorus, arsenic, antimony and bismuth from Group Va. These materials can be substituted in the metallo nucleus with a wide variety of substituents but at least one of the substituents must be an amino-aryl radical. The amino radical can be positioned anywhere on the aromatic nucleus, but best results are obtained if the aryl moiety is a phenyl radical having the amino group in the 4 or para position. Typical substituents attached to the metal nucleus include the following:

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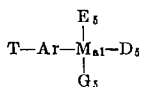
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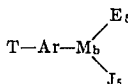
1. a hydrogen, sulfur or oxygen atom,
2. an alkyl radical,

3. an aryl radical including unsubstituted as well as substituted aryl radicals such as aminoaryl, alkylaryl and haloaryl,
4. an oxygen-containing radical such as an alkoxy or aryloxy radical,
5. an amino radical including unsubstituted and substituted amino radicals such as mono- and diarylamino and mono- and dialkylamino radicals,
6. a heterocyclic radical, and
7. a Group IVa or Va organo metallic radical. Photoconductors included in this class can be represented by the following structures:

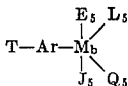
1.



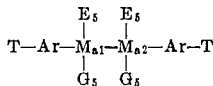
2.



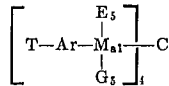
3.



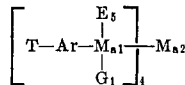
4.



5.



6.



where  $E_5$ ,  $G_5$ ,  $L_5$  and  $Q_5$  can be:

- a. a hydrogen atom,
- b. an aryl radical including unsubstituted as well as substituted aryl radicals such as a phenyl radical, a naphthyl radical, a dialkylaminophenyl radical, or a diarylamino phenyl radical,
- c. an alkyl radical having one to eight carbon atoms,
- d. an alkoxy radical having one to eight carbon atoms,
- e. an aryloxy radical such as a phenoxy radical,
- f. an amino radical having the formula



wherein  $R_{21}$  and  $R_{22}$  can be hydrogen atoms or alkyl radicals having one to eight carbon atoms, or

- g. a heterocyclic radical having five to six atoms in the hetero nucleus including at least one nitrogen atoms such as a triazolyl, a pyridyl radical, etc.,

T is an amino radical such as an alkylamino radical having one to eight carbon atoms or an arylamino radical such as a phenylamino radical;

Ar is an aromatic radical such as phenyl or naphthyl;

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

$M_b$  is a Group Va metal;

$D_5$  can be any of the substituents set forth above for  $E_5$ ,  $G_5$ ,  $L_5$  and  $Q_5$  and in addition can be a Group IVa organo-metallic radical or, when taken with E, an oxygen atom or a sulfur atom;

$J_5$  can be any of the substituents set forth above for  $E_5$ ,  $G_5$ ,  $L_5$  and  $Q_5$  and in addition can be when taken with E, an oxygen atom or a sulfur atom. These materials are described in U.S. Ser. No. 650,664 filed July 3, 1967.

K. Any other organic compound which exhibits photoconductive properties such as those set forth in Australian Pat. No. 248,402.

- 5 Representative organic photoconductors useful in this invention include the compounds listed below:

TABLE I

	diphenylamine
	dinaphthylamine
10	N,N'-diphenylbenzidine
	N-phenyl-1-naphthylamine
	N-phenyl-2-naphthylamine
	N,N'-diphenyl-p-phenylenediamine
15	2-carboxy-5-chloro-4'-methoxydiphenylamine
	p-anilinophenol
	N,N'-di-2-naphthyl-p-phenylenediamine
	4,4'-benzylidene-bis-(N,N-dimethyl-m-toluidine)
	triphenylamine
20	N,N,N',N'-tetraphenyl-m-phenylenediamine
	4-acetyltriphenylamine
	4-hexanoyltriphenylamine
	4-lauroyltriphenylamine
	4-hexyltriphenylamine
25	4-dodecyltriphenylamine
	4,4'-bis(diphenylamino)benzil
	4,4'-bis(diphenylamino)benzophenone
	poly[N,4''-(N,N',N'-triphenylbenzidine)]
	polyadipyltriphenylamine
30	polysebacyltriphenylamine
	polydecamethylenetriphenylamine
	poly-N-(4-vinylphenyl)diphenylamine
	poly-N-(vinylphenyl)- $\alpha,\alpha'$ -dinaphthylamine
	4,4'-benzylidene-bis(N,N-diethyl-m-toluidine)
35	4',4''-diamino-4-dimethylamino-2',2''-dimethyltriphenylmethane
	4',4''-bis(diethylamino)-2,6-dichloro-2',2''-dimethyltriphenylmethane
	4',4''-bis(diethylamino)-2',2''-dimethyl-4-dimethyldiphenylnaphthylmethane
40	2',2''-dimethyl-4,4',4''-tris(dimethylamino)triphenylmethane
	4',4''-bis(diethylamino)-4-dimethylamino-2',2''-dimethyltriphenylmethane
	4',4''-bis(diethylamino)-2-chloro-2',2''-dimethyl-4-dimethylaminotriphenylmethane
45	4',4''-bis(diethylamino)-4-dimethylamino-2,2',2''-trimethyltriphenylmethane
	4',4''-bis(dimethylamino)-2-chloro-2',2''-dimethyltriphenylmethane
50	4',4''-bis(dimethylamino)-2',2''-dimethyl-4-methoxytriphenylmethane
	bis(4-diethylamino)-1,1,1-triphenylethane
	bis(4-diethylamino)tetraphenylmethane
55	4',4''-bis(benzylethylamino)-2',2''-demethyltriphenylmethane
	4',4''-bis(diethylamino)-2',2''-diethoxytriphenylmethane
	4,4'-bis(dimethylamino)-1,1,1-triphenylethane
	1-(4-N,N-dimethylaminophenyl)-1,1-diphenylethane
60	4-dimethylaminotetraphenylmethane
	4-diethylaminoetraphenylmethane
	4,4'-bis(diphenylamino)chalcone
	4-diphenylamino-4'-dimethylaminochalcone
	4-dimethylamino-4'-diphenylaminochalcone
65	4,4'-bis(dimethylamino)chalcone
	4,4'-bis(diethylamino)chalcone
	4-diethylamino-4'-diphenylaminochalcone
	4-diphenylaminochalcone
	4-dimethylaminochalcone
	4'-diphenylaminochalcone
	4'-dimethylaminochalcone
70	bis-[5-(5H-dibenzo[a,d]cycloheptenyl)]ether
	5-hydroxy-5H-dibenzo[a,d]cycloheptene
75	1-{5-(5H-dibenzo[a,d]cycloheptenyl)}-4,5-dicarbomethoxy-1,2,3-triazole

1-{5-(5H-dibenzo[a,d]cycloheptenyl)}-4,5-dibenzoyl-1,2,3-triazole  
 5-azido-5H-dibenzo[a,d]cycloheptene  
 1-{5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)} 4,5-dicarbomethoxy-1,2,3-triazole  
 1-{5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)} 4,5-dibenzoyl-1,2,3-triazole  
 4-[5-(5H-dibenzo[a,d]cycloheptenyl)-N,N-dimethylaniline  
 N,N-diethyl-3-methyl-4-[5-(5H-dibenzo[a,d]cycloheptenyl)]aniline  
 4-[5-(5H-dibenzo[a,d]cycloheptenyl)]-1-dimethylaminonaphthalene  
 N,N-diethyl-3-methyl-4-[5-(10,11-dihydro-5H-dibenzo[a,d]cycloheptenyl)]aniline  
 3-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene  
 3-(4-diethylamino-2-methylphenyl)-1,3,5-cycloheptatriene  
 3-(4-dimethylaminoaphthyl)-1,3,5-cycloheptatriene  
 N,N-diethyl-3-methyl-4-[5-(5H-dibenzo[a,d]cycloheptenyl)]aniline  
 tetra- $\alpha$ -naphthylhydrazine  
 tetra(3-methyl-4-hydroxyphenyl)hydrazine  
 tetra(m-hydroxyethylphenyl)hydrazine  
 tetra(2-methyl-5-chloroethylphenyl)hydrazine  
 tetra(2-methyl-5-hydroxyphenyl)hydrazine  
 tetra(1-imidazolyl)hydrazine  
 N,N-di- $\alpha$ -naphthyl-N',N'-di(3-methyl-4-hydroxyphenyl)hydrazine  
 N-3-furyl-N-(2-methyl-4-hydroxyphenyl)-N',N'-di- $\beta$ -naphthylhydrazine  
 tetra- $\beta$ -naphthylhydrazine  
 N,N'-di- $\beta$ -naphthyl-N,N'-diphenylhydrazine  
 tetra-4-tolylhydrazine  
 N,N'-diphenyl-N,N'-di(3-methyl-4-hydroxyphenyl)hydrazine  
 N,N'-diphenyl-N,N'-di-p-chlorophenyl hydrazine  
 phenyltri-(2-methyl-5-hydroxyphenyl)hydrazine  
 N,N'-bicarbazyl  
 cyclotetrakis(3,9-carbazolyene)  
 6-(3-carbazolyl)-cyclotetrakis(3,9-carbazolyene)  
 6-(9-carbazolyl)-cyclotetrakis(3,9-carbazolyene)  
 3,3'-bis(3-carbazolyl)-9,9'-bicarbazolyl  
 3-(3-carbazolyl)-9-(9-carbazolyl)carbazole  
 3-(9-carbazolyl)-9,9'-bicarbazolyl  
 3,3'-diethyl-9,9'-bicarbazolyl  
 3,3'-diphenyl-9,9'-bicarbazolyl  
 3,3'-dichloro-9,9'-bicarbazolyl  
 4,4'-bis(diethylamino)-9,9'-bicarbazolyl  
 3,3'-diethoxy-9,9'-bicarbazolyl  
 1,1'-dihydroxy-9,9'-bicarbazolyl  
 2,2'-dicyano-9,9'-bicarbazolyl  
 tetra(p-diethylaminophenyl)hydrazine  
 3,3'-bis(1,5-diphenyl-2-pyrazoline)  
 3,3'-bis(1-p-tolyl-5-phenyl-2-pyrazoline)  
 3,3'-bis(1,5-diphenyl-4-dimethylamino-2-pyrazoline)  
 3,3'-bis[1,5-diphenyl-4-(p-chlorophenyl)-2-pyrazoline]  
 3,3'-bis[1,5-diphenyl-4,5-di-(p-diethylaminophenyl)-2-pyrazoline]  
 3,3'-bis[1,5-diphenyl-4-(p-methoxyphenyl)-5-ethyl-2-pyrazoline]  
 3,3'-bis(1,5-diphenyl-4-chloromethyl-2-pyrazoline)  
 1,5-diphenyl-4,5-dimethyl-3-[3'-(1'-p-tolyl-4'-diethyl-5',5'-methylphenyl)-2'-pyrazolyl]-2-pyrazoline  
 4-(p-diphenylaminophenyl)-3-buten-1-yne  
 p-diphenylaminostyrene  
 ethyl p-diphenylaminocinnamate  
 methyl p-diphenylaminocinnamate  
 p-diphenylaminocinnamoyl chloride  
 p-diphenylaminocinnamic acid  
 N,N-diphenylamide  
 p-diphenylaminocinnamic acid anhydride

3-(p-diphenylaminophenyl)-2-butenic acid  
 bis(p-diphenylaminobenzal)succinic acid  
 4-N,N-bis(p-bromophenyl)aminocinnamic acid  
 1-(4-diphenylamino)naphthacrylic acid  
 5 p-diphenylaminocinnamic acid  
 p-diphenylaminocinnamoyl chloride  
 7-diphenylamino coumarin  
 p-diphenylaminophenylvinylacrylic acid  
 10 p-diphenylaminobenzyl p'-diphenylaminocinnamate  
 7-(p-diphenylaminostyryl)coumarin  
 p-diphenylaminocinnamyl alcohol  
 4-diphenylaminocinnamaldehyde semicarbazone  
 O-p-diphenylaminocinnamoyl p'-diphenylaminobenzaldehyde oxime  
 15 p-diphenylaminocinnamaldehyde oxime  
 1,3-bis(p-diphenylaminophenyl)-2-propen-1-ol  
 methyl p-diphenylaminobenzoate  
 N,N-diphenylanthranilic acid  
 3-p-diphenylaminophenyl-1-propanol  
 20 4-acetyltriphenylamine semicarbazone  
 ethyl 2,6-diphenyl-4-(p-diphenylaminophenyl)benzoate  
 1-(p-diphenylaminophenyl)-1-hydroxy-3-butyne  
 4-hydroxymethyltriphenylamine  
 25 1-(p-diphenylaminophenyl)ethanol  
 4-hydroxytriphenylamine  
 2-hydroxytriphenylamine  
 4-formyltriphenylamine oxime  
 4-acetyltriphenylamine oxime  
 30 1-(p-diphenylaminophenyl)hexanol  
 1-(p-diphenylaminophenyl)dodecanol  
 p-diphenylaminobenzoic acid anhydride  
 4-cyanotriphenylamine  
 p-diphenylaminobenzoic acid  
 N,N-diphenylamide  
 35 p-diphenylaminobenzoic acid  
 p-diphenylaminobenzoyl chloride  
 3-p-diphenylaminophenylpropionic acid  
 4-formyltriphenylamine semicarbazone  
 40 triphenyl-p-diethylaminophenylsilane  
 methyl-diphenyl-p-diethylaminophenylsilane  
 triphenyl-p-diethylaminophenylgermane  
 triphenyl-p-dimethylaminophenylstannane  
 triphenyl-p-diethylaminophenylstannane  
 diphenyl-di-(p-diethylaminophenyl)stannane  
 45 triphenyl-p-diethylaminophenylplumbane  
 tetra-p-diethylaminophenylplumbane  
 phenyl-di-(p-diethylaminophenyl)phosphine  
 bis(p-diethylaminophenyl)phosphine oxide  
 tri-p-dimethylaminophenylarsine  
 50 tri-p-diethylaminophenylarsine  
 2-methyl-4-dimethylaminophenylarsine oxide  
 tri-p-diethylaminophenylbismuthine  
 methyl-di-(p-diethylaminophenyl)arsine  
 methyl-di-(p-diethylaminophenyl)phosphine  
 phenyl-tri(p-diethylaminophenyl)stannane  
 55 methyl-tri(p-diethylaminophenyl)stannane  
 tetra-p-diethylaminophenylgermane  
 diphenyl-p-diethylaminophenylsilane  
 p-diethylaminophenylarsine  
 60 tetrakis-[diphenyl-(p-diethylaminophenyl)plymbyl]methane  
 tetrakis-[diphenyl-(p-diethylaminophenyl)stannyl]stannane  
 bis-[phenyl-(p-diethylaminophenyl)]dibismuthine  
 65 tri-(p-diethylaminophenyl)phosphine sulfide  
 di-(p-diethylaminophenyl)thioxotin  
 Preferred binders for use in preparing the present photoconductive layers are film-forming, 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; soyaalkyd 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(methyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as copoly[ethylene-co-alkylenebis(alkyleneoxyaryl)phenylenedicarboxylate]; phenolformaldehyde resins; ketone resins; polyamides; polycarbonates; polythiocarbonates; poly[ethylene-co-isopropylidene-2,2-bis(ethyleneoxyphenylene)terephthalate]; copolymers of vinyl haloarylates and vinyl acetate such as poly(vinyl m-bromobenzoate-co vinyl acetate); 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 trade-names 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. Mixtures of these binders may also be employed.

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

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

Suitable supporting materials for the photoconductive layers of the present invention can include any of a wide variety of electrically conducting supports, for example, various-conducting papers; 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 support material such as poly(ethylene terephthalate) with a layer containing a semiconductor dispersed in a resin. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. No. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxy-ester lactone of a maleic anhydride-vinyl acetate copolymer. Such kinds of 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 elements of the present invention can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the aforementioned xerographic process. As explained previously, in a process of this type the electrophotographic element is given a

blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer owing to the substantial insulating property of the layer, i.e., the conductivity of the layer in the dark. The electrostatic charge formed on the surface of the photoconducting layer is then selectively dissipated from the surface of the layer by exposure to light through an image-bearing transparency by a conventional exposure operation such as, for example, by contact-printing technique, or by lens projection of an image, etc., to form a charge image in the photoconducting layer. By exposure of the surface in this manner, a charge pattern is created by virtue of the fact that light causes the charge to be conducted away in proportion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then developed, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust, e.g., powder, a pigment in a resinous carrier, i.e., toner, or a liquid developer may be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature in such patents, for example, as U.S. Pat. No. 2,297,691, and in Australian Pat. No. 212,315. In processes of electrophotographic reproduction such as in xerography, by selecting a developing particle which has as one of its components, a low-melting resin, it is possible to treat the developed photoconductive material with heat and cause the powder to adhere permanently to the surface of the photoconductive layer.

The present invention is not limited to any particular mode of use of the new electrophotographic materials, and the exposure technique, the charging method, the transfer (if any), the developing method, and the fixing method as well as the material used in these methods can be selected and adapted to the requirements of any particular technique.

#### EXAMPLE 1

A composition in the form of a dope consisting of the following materials is coated at a wet thickness of 0.004 inch on a poly(ethylene terephthalate) film support having a conducting layer of the sodium salt of butyl ester lactone made from vinyl acetate - maleic anhydride copolymer as in Example 1 of U.S. Pat. No. 3,260,706:

Photoconductor. 3-(4-diphenylaminophenyl) propionic acid	0.5 g.
Binder. poly(4,4'-isopropylidene-bisphenyleneoxyethylene-co-ethylene isophthalate)	1.5 g.
Sensitizer I	0.01 g.
Dichloromethane	9.60 g.

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 charge image is developed by cascading over the surface of the layer negatively charged black thermoplastic toner particles on glass bead carriers. The background area of the reproduction is a deep red, causing the developed image to have very poor visual contrast. The developed image-bearing element is then exposed to the radiation from a 500 watt G.E. lamp (No. PH/RFL2) at a distance of 5 inches for 25 seconds. The deep red color bleached to a pale yellow and the developed image has a substantially improved visual contrast.

## EXAMPLE 2

Example 1 is repeated except bleaching is accomplished by heating the developed image-bearing element at 140° C. for 60 seconds. The bleached element has an improved visual contrast compared to the unbleached element.

## EXAMPLE 3

Examples 1 and 2 are repeated, simultaneously heating to 125° C. and exposing the developed image bearing element to the 500 watt source to cause bleaching. Substantial bleaching to a pale yellow is caused within 15 seconds. The developed image is easily viewable.

## EXAMPLE 4

Example 1 is repeated using the following photoconducting compounds in place of 3-(4-diphenylaminophenyl) propionic acid:

- a. 4-carboxytriphenylamine,
- b. 3-(4-diphenylamino)phenyl methyl propionate and
- c. bis-4-diethylaminotetraphenylmethane.

The binder is replaced with poly(vinyl-m-bromobenzoate-co-vinyl acetate). After bleaching each of the elements in the described manner, good quality images having good visual contrast are obtained in each instance.

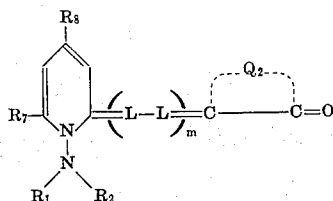
## EXAMPLE 5

Example 1 is repeated except the sensitizer is omitted. No developable electrostatic charge image is obtained.

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 photoconductor and a 1-aminopyridinium dye sensitizer for said composition, said sensitizer having the formula:



wherein:

Q<sub>2</sub> represents the non-metallic atoms necessary to complete a five to six membered heterocyclic nucleus;

R<sub>1</sub> and R<sub>2</sub> when taken separately are each selected from the group consisting of

- a. an alkyl group,
- b. an acyl group,
- c. hydrogen,
- d. an aryl group,
- e. a heterocyclic nucleus containing five to six members in the hetero nucleus, and
- f. when taken together represent the atoms necessary to complete a five to six membered heterocyclic nucleus;

R<sub>7</sub> and R<sub>8</sub> are each selected from the group consisting of

- a. a hydrogen atom,
- b. an alkyl group, and
- c. an aryl group;

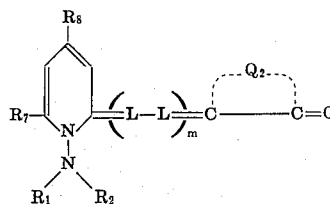
m is a positive integer from 1 to 2; and

L is a methine linkage.

2. The composition of claim 1 wherein the photoconductor is an organic compound.

3. The composition of claim 1 further comprising a polymeric film-forming binder.

4. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising an organic photoconductor and a sensitizer for said photoconductive composition having the formula:



wherein:

Q<sub>2</sub> represents the non-metallic atoms necessary to complete a five to six membered heterocyclic nucleus;

R<sub>1</sub> and R<sub>2</sub> when taken separately are each selected from the group consisting of

- a. an alkyl group,
- b. an acyl group,
- c. hydrogen,
- d. an aryl group,
- e. a heterocyclic nucleus containing five to six members in the hetero nucleus, and
- f. when taken together represent the atoms necessary to complete a five to six membered heterocyclic nucleus;

R<sub>7</sub> and R<sub>8</sub> are each selected from the group consisting of

- a. a hydrogen atom,
- b. an alkyl group, and
- c. an aryl group;

m is a positive integer from 1 to 2; and

L is a methine linkage.

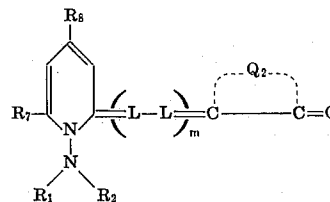
5. The element of claim 4 wherein the photoconductive composition contains a polymeric film-forming binder.

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

- a. about 10 percent to about 60 percent by weight based on said photoconductive composition of an organic photoconductor,
- b. a film-forming polymeric binder for said photoconductor and
- c. 0.005 percent to about 5 percent by weight based on said photoconductive composition of a sensitizer comprising 3-[(1-{N-methylanilino}-4,6-di-p-tolyl-2(1H)-pyridylidene]ethylidene)-2H-pyrido[1,2-a]pyrimidine-2,4-(3H)-dione.

7. The element of claim 6 wherein said organic photoconductor is 3-(4-diphenylaminophenyl)propionic acid.

8. A process for bleaching an image-bearing electrophotographic element having a layer of a photoconductive composition containing a 1-aminopyridinium dye sensitizer comprising the step of heating the element to a temperature of at least about 140° C. for at least about 15 seconds, said sensitizer having the formula:



65 wherein:

Q<sub>2</sub> represents the non-metallic atoms necessary to complete a five to six membered heterocyclic nucleus;

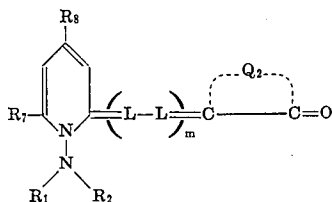
R<sub>1</sub> and R<sub>2</sub> when taken separately are each selected from the group consisting of

- a. an alkyl group,
- b. an acyl group,
- c. hydrogen,
- d. an aryl group,
- e. a heterocyclic nucleus containing five to six members in the hetero nucleus, and

- f. when taken together represent the atoms necessary to complete a five to six membered heterocyclic nucleus;
- $R_7$  and  $R_8$  are each selected from the group consisting of
- a hydrogen atom,
  - an alkyl group, and
  - an aryl group;
- $m$  is a positive integer from 1 to 2; and  
 $L$  is a methine linkage.

9. The process of claim 8 further comprising simultaneously exposing the element to an illuminance of at least 4,000 foot-candles during the heating step.

10. A process for bleaching an image-bearing electrophotographic element having a layer of a photoconductive composition containing a 1-aminopyridinium dye sensitizer, comprising the step of subjecting the element to actinic radiation of at least about  $6 \times 10^4$  foot-candles-seconds and to which the element is sensitive, said sensitizer having the formula:



wherein:

$Q_2$  represents the non-metallic atoms necessary to complete a five to six membered heterocyclic nucleus;

5  $R_1$  and  $R_2$  when taken separately are each selected from the group consisting of

- an alkyl group,
- an acyl group,
- hydrogen,
- an aryl group,

10 e. a heterocyclic nucleus containing five to six members in the hetero nucleus, and

f. when taken together represent the atoms necessary to complete a five to six membered heterocyclic nucleus;

15  $R_7$  and  $R_8$  are each selected from the group consisting of

- a hydrogen atom,
- an alkyl group, and
- an aryl group;

$m$  is a positive integer from 1 to 2; and

20  $L$  is a methine linkage.

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