



### 9,10-SUBSTITUTED ACRIDINES AS SENSITIZERS IN ELECTROPHOTOGRAPHIC SYSTEMS

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 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 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 latent 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 wavelength 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 wavelength 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.

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.

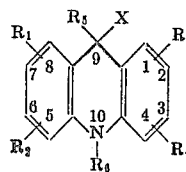
It is a further object of this invention to provide a process for using novel sensitized photoconductive elements.

These and other objects are accomplished with photoconductive compositions containing a photoconductor and a sensitizer which is a nuclear-substituted acridine having substituents in the 9 and 10 positions. Typical of such nuclear substituents include substituted and unsubstituted alkyl groups and substituted and unsubstituted aryl groups. The photoconductor can be either an organic or an inorganic photoconductor.

A large number of acridine compounds have exhibited some degree of sensitization when used as sensitizers in photoconductive compositions. Typical of these are acriflavine, acridine orange, benzoflavine, rheonine and flavophosphine as described in U.S. Pat. No. 3,316,087 and French Pat. No. 1,288,392. These compounds, none of which is substituted in both the 9 and 10 positions, have routinely been used as sensitizers. According to this invention, it has surprisingly been found that when substituents are placed in the 9 and 10 positions of the acridine nucleus, an enhanced sensitization effect is realized when these materials are used in a photoconductive composition in comparison to the sensitization effect attained from those traditionally used acridines. This enhanced sensitization is evidenced by greater electrical speeds. In particular, substantial increases in speeds are obtained as compared to speeds attainable with many other closely related sensitizing compounds, including those acridines which do not contain substituents in both the 9 and 10 positions. These increases in speed are observed when the coating accepts a suitable potential (e.g., 500-600 volts) and the relative speed of the coating is determined on the basis of the reciprocal of the exposure required to reduce the potential of the surface charge by 100 volts (shoulder speed) or to 100 volts (toe speed). The terms "shoulder speed" and "toe speed" are terms known in the silver halide photographic art with reference to "H and D" curves. As used herein, such terms refer to related curves resulting from exposure plotted against voltage. The reduction of the surface potential to 100 volts or below is significant in that represents a requirement for suitable broad area development of an electrostatic image. The relative speed at 100 volts is a measure of the ability to produce and hence to develop or otherwise utilize the electrostatic latent image. When the sensitizer is absent from the coating and only a photoconductor is used, the surface potential usually does not drop to or below 100 volts and therefore no speed can be assigned to such a composition. When a sensitizer is part of the coating in many compositions containing conventional polymeric binders and photoconductors, the surface potentials of such resultant compositions usually drop below 100 volts, and thus, a definite speed can be ascertained. However, these speeds are improved when the sensitizers of this invention are employed.

The 9, 10-disubstituted acridine compounds can be made to absorb radiation over various ranges of the spectrum by varying the substituents and thereby provide sensitivity of the electrophotographic system or other light-sensitive system to various wavelengths of radiation as might be required by different practice applications. These compounds have the advantage of providing a high level of efficiency in contrast to some other sensitizers. They are also markedly stable so that undesirable bleaching or other changes in the absorption of radiation by the light-sensitive system are not encountered.

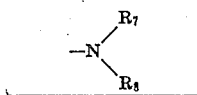
The preferred acridine sensitizers of this invention are characterized by the following structure:



wherein

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  can be any of the following substituents:  
a. hydrogen

- b. an alkyl group preferably having one to eight carbon atoms including a substituted alkyl group such as aralkyl, aminoalkyl, hydroxyalkyl, carboxyalkyl, haloalkyl, alkoxyalkyl, aryloxyalkyl, nitroalkyl, etc.;
- c. an amino group including a substituted amino group, e.g.,



wherein  $R_7$  and  $R_8$  are either hydrogen, alkyl containing one to eight carbon atoms, aryl, etc.;

- d. halogen such as chlorine, bromine, fluorine, iodine;
- e. an aryl group such as phenyl or naphthyl, including a substituted aryl group such as alkaryl, aminoaryl, hydroxyl, alkoxyaryl, carboxyaryl, haloaryl, nitroaryl, cyanoaryl, etc.;
- f. an alkenyl group preferably having two to eight carbon atoms including a substituted alkenyl group such as aminoalkenyl, haloalkenyl, nitroalkenyl, etc.;
- g. an alkoxy group preferably having one to eight carbon atoms including a substituted alkoxy group such as aminoalkoxy, haloalkoxy, arylalkoxy, nitroalkoxy, hydroxyalkoxy, etc.;
- h. an aryloxy group including a substituted aryloxy group such as alkaryloxy e.g., methylphenoxy, aminoaryloxy, haloaryloxy, etc.;
- i. a nitro group;
- j. a hydroxy group;
- k. a cyano group; and
- l. an acyl group including a substituted acyl group such as



wherein  $R_9$  can be an alkyl group having one to eight carbon atoms, hydrogen, amino, halogen, aryl, alkoxy, hydroxy, etc.;

$R_3$  and  $R_6$  can be either (a) an alkyl group preferably having one to eight carbon atoms including a substituted alkyl group such as aralkyl, aminoalkyl, hydroxyalkyl, carboxyalkyl, haloalkyl, alkoxyalkyl, aryloxyalkyl, nitroalkyl, etc., or (b) an aryl group including a substituted aryl group such as phenyl, naphthyl, alkaryl, aminoaryl, hydroxyaryl, alkoxyaryl, carboxyaryl, haloaryl, nitroaryl, cyanoaryl, etc. and

X is a substituent which is dissociated to some extent as an anion such as halogen, sulfate, perchlorate, fluoroborate, chloroplatinate, hexafluorophosphate, p-toluenesulfonate, trifluoroacetate, hydroxy, alkoxy, picrate, etc.

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

- I. 9-(4-Dimethylaminophenyl)-10-phenyl-9-acridanol
- II. 9-(4-Dimethylaminophenyl)-10-phenylacridinium diperchlorate
- III. 9-(4-Dimethylaminophenyl)-10-phenylacridinium ditrifluoroacetate
- IV. 9,10-Diphenyl-9-acridanol
- V. 9,10-Diphenylacridinium perchlorate
- VI. 9,10-Diphenylacridinium ditrifluoroacetate
- VII. 9,10-Diphenylacridinium fluoroborate
- VIII. 9,10-Diphenylacridinium hexafluorophosphate
- IX. 9-(4-Dimethylaminophenyl)-10-phenylacridinium chloride
- X. 9-Phenyl-10-methylacridinium perchlorate
- XI. 9-Phenyl-10-methylacridinium fluoroborate
- XII. 9-(4-Dimethylaminophenyl)-10-methylacridinium iodide
- XIII. 9-Phenyl-10-benzylacridinium fluoroborate
- XIV. 9-Phenyl-10-benzylacridinium perchlorate
- XV. 9-(4-Dimethylaminophenyl)-10-methylacridinium diperchlorate
- XVI. 9-(4-Dimethylaminophenyl)-10-methylacridinium difluoroborate

- XVII. 9-(4-Dimethylaminophenyl)-10-methylacridinium perchlorate
- XVIII. 9-(4-Dimethylaminophenyl)-10-methylacridinium fluoroborate
- XIX. 9-(4-Dimethylaminophenyl)-9-ethoxy-10-benzylacridane
- XX. 9-(4-Dimethylaminophenyl)-10-benzylacridinium diperchlorate
- XXI. 9-(4-Dimethylaminophenyl)-10-benzylacridinium difluoroborate
- XXII. 9-(4-Dimethylaminophenyl)-10-benzylacridinium perchlorate
- XXIII. 9-(4-Dimethylaminophenyl)-10-benzylacridinium fluoroborate
- XXIV. 2-Chloro-9,10-diphenylacridol
- XXV. 3-Chloro-9,10-diphenylacridol
- XXVI. 10-Phenyl-9-(2-chlorophenyl)acridol
- XXVII. 10-Phenyl-9-(3-chlorophenyl)acridol
- XXVIII. 10-Phenyl-9-(4-chlorophenyl)acridol
- XXIX. 10-(4-chlorophenyl)-2-chloro-9-phenylacridol
- XXX. 10-Methyl-9-methylacridinium iodide
- XXXI. 10-methyl-9-ethylacridinium iodide
- XXXII. 10-Methyl-9phenylacridinium chloride
- XXXIII. 10-Methyl-9-phenylacridinium ferrichloride
- XXXIV. 10-Methyl-9-phenylacridinium iodide
- XXXV. 10-Methyl-9-phenylacridinium mercurichloride
- XXXVI. 10-Methyl-9-phenylacridinium perchlorate
- XXXVII. 10-Methyl-9-phenylacridinium picrate
- XXXVIII. 10-Methyl-9-m-tolylacridinium picrate
- XXXIX. 10-Methyl-9-p-tolylacridinium picrate
- XL. 10-Methyl-9-p-chlorophenylacridinium iodide
- XLI. 10-Methyl-9-p-bromophenylacridinium iodide
- XLII. 10-Methyl-9-(p-dimethylaminophenyl)acridol
- XLIII. 10-Methyl-9-p-dimethylaminophenyl)acridinium chloride
- XLIV. 10-Methyl-9-(p-dimethylaminophenyl)acridinium nitrate
- XLV. 10-Methyl-9-(p-hexyloxyphenyl)acridol
- XLVI. 10-Methyl-9-(p-hexyloxyphenyl)acridinium chloride
- XLVII. 10-Ethyl-9-phenylacridinium iodide
- XLVIII. 2-Methyl-9,10-diphenylacridol
- XLIX. 3-Dimethylamino-9,10-diphenylacridol
- L. 3,9,10-triphenylacridol
- LI. 2-Styryl-9,10-diphenylacridol
- LII. 3-Ethoxy-9,10-diphenylacridol
- LIII. 3-Phenoxy-9,10-diphenylacridol
- LIV. 3-Nitro-9,10-diphenylacridol
- LV. 2-Hydroxy-9,10-diphenylacridol
- LVI. 3-Cyano-9,10-diphenylacridol
- LVII. 3-Formyl-9,10-diphenylacridol
- LVIII. 3-Carboxy-9,10-diphenylacridol
- LIX. 9-Phenyl-10-p-tolyl-2,7-dimethylacridol
- LX. 9,10-di-p-tolyl-2,7-dimethylacridol
- 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

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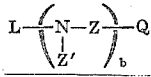
composition in an amount from about 0.005 to about 5.0 percent by weight of the total coating composition.

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 cadmium sulfide and the like and organic photoconductors including organometallic photoconductors

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 tetraarylmethanes 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 nonleuco base materials; and also other polyaryllkanes included by the formula:



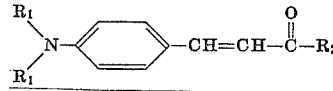
wherein each of D, E and G is an aryl group and J is a hydrogen atom, an alkyl group, or an aryl group, at least one of D, E and G containing an amino substituent, the aryl groups attached to the central carbon atom being preferably phenyl groups, although naphthyl groups can also be used including substituted 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

6

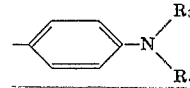


5 wherein each R can be an alkyl group typically having one to eight carbon atoms, a hydrogen atom, an aryl group, or together the necessary atoms to form a heterocyclic amino group typically having 5 to 6 atoms in the ring such as morpholino, pyridyl, pyrrol, etc.; at least one of D, E and G preferably 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. Pat. Ser. No. 627,857 filed Apr. 3, 1967 by Seus and Goldman now U.S. Pat. No. 3,542,544.

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

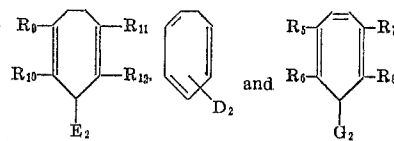


wherein R<sub>1</sub> and R<sub>2</sub> are each phenyl radicals including substituted phenyl radicals, R<sub>2</sub> preferably having the formula



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. Pat. Ser. No. 613,946 now U.S. Pat. No. 3,526,501.

E. Non-ionic cycloheptenyl compounds which may be substituted with substituents such as (a) an aryl radical including substituted as well as unsubstituted aryl radicals, (b) a hydroxy radical, (c) a heterocyclic radical, (d) a heterocyclic radical having 5 to 6 atoms in the heterocyclic nucleus and at least one hetero nitrogen atom, and including substituted and unsubstituted heterocyclic radicals, and (e) 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<sub>2</sub> and G<sub>2</sub> can be either:

- a phenyl radical,
- a naphthyl radical,
- a heterocyclic radical having 5 to 6 atoms in the heterocyclic nucleus and at least 1 hetero nitrogen atom,
- a hydroxyl radical, or
- an oxygen containing radical having a structure such that the resultant cycloheptenyl compound is a symmetrical ether; D<sub>2</sub> can be any of the substituents defined for E<sub>2</sub> and G<sub>2</sub> above and is attached to a carbon atom in the cycloheptenyl nucleus having a double bond; (R<sub>9</sub> and R<sub>10</sub>), (R<sub>11</sub> and R<sub>12</sub>), (R<sub>5</sub> and R<sub>6</sub>), and (R<sub>7</sub> and R<sub>8</sub>) are together the necessary atoms to complete a benzene ring fused to the cycloheptenyl nucleus; these compounds

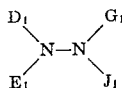
being more fully described in U.S. Pat. Ser. No. 654,091 filed July 18, 1967.

F. Compounds containing an



nucleus including (1) unsubstituted and substituted N,N-bicarbazyls N-bicarbazyls containing substituents in either or both carbazoyl nuclei such as

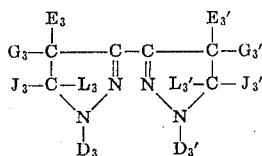
- a. an alkyl radical including a substituted alkyl radical such as a haloalkyl or an alkoxyalkyl radical,
- b. a phenyl radical including a substituted phenyl radical such as a naphthyl, an aminophenyl or a hydroxyphenyl radical,
- c. a halogen atom,
- d. an amino radical including substituted as well 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, a carbazolyl or a pyridyl radical; or (2) tetra-substituted hydrazines containing substituents which are substituted or unsubstituted phenyl radicals, or heterocyclic radicals having 5 to 6 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 5 to 6 atoms in the hetero nucleus. Other tetra-substituted hydrazines include those having the following formula:



wherein D<sub>1</sub>, E<sub>1</sub>, G<sub>1</sub> and J<sub>1</sub> are each either

- a. a substituted phenyl radical such as a naphthyl radical, an alkylphenyl 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<sub>1</sub> and E<sub>1</sub> can also be
- c. an unsubstituted phenyl radical. Especially preferred are those tetra-substituted hydrazines wherein both D<sub>1</sub> and G<sub>1</sub> are either substituted phenyl radicals or heterocyclic radicals. These compounds are more fully described in U.S. Pat. Ser. No. 673,962 filed Oct. 9, 1967 now U.S. Pat. No. 3,542,546.

G. Organic compounds having a 3,3'-bis-aryl-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<sub>3</sub>, D<sub>3</sub>', J<sub>3</sub> and J<sub>3</sub>' can be either a phenyl radical including a substitute phenyl radical such as a tolyl radical or a naphthyl radical including a substituted naphthyl radical,

E<sub>3</sub>, E<sub>3</sub>', G<sub>3</sub>, G<sub>3</sub>', L<sub>3</sub> and L<sub>3</sub>' can be any of the substituents set forth above and in addition can be either a hydrogen atom or an alkyl radical containing one-eight carbon atoms. These organic photoconductors are more fully described in U.S. Pat. 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 CH=CH<sub>n</sub> wherein n is an integer of from one to three. 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:

- a. carboxy radicals,
- b. hydroxy radicals,
- c. ethynyl radicals,

(d) ester radicals (e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}_{13}$  wherein R<sub>13</sub> is alkyl or aryl) including cyclic ester radicals (e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}_{14}$  wherein R<sub>14</sub>

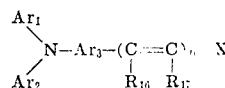
is a cyclic alkylene radical connected to a vinylene combination such as is found in coumarin derivatives),

- e. carboxylic acid anhydride radicals,
- f. semicarbazono radicals,
- g. cyano radicals,

(h) acyl halide radicals e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$  etc.), and

(i) amido radicals (e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{array}{l} \text{R}_{15} \\ \text{R}_{16} \end{array}$  wherein R<sub>15</sub> is a

hydrogen atom, an alkyl group or an aryl group). Other active hydrogen-containing groups include substituted and unsubstituted alkyldiene oximido radicals. Photoconductors included in this class can be represented by the following structure:



wherein:

- a. Ar<sub>1</sub> and Ar<sub>2</sub> are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an aminophenyl radical;
- b. Ar<sub>3</sub> is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical,
- c. R<sub>16</sub> and R<sub>17</sub> are each hydrogen, a phenyl radical including a substituted phenyl radical or a lower alkyl radical preferably having one to eight carbon atoms;
- d. X is either (1) 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 methyldiene oximido radical, or (2) hydrogen, provided that when X is hydrogen R<sub>16</sub> and R<sub>17</sub> are also hydrogen; and

e.  $n$  is an integer of one to three. The arylene nucleus can be substituted in any position by the vinyl or vinylene moiety. However, when  $Ar_3$  is phenylene, particularly good results are obtained if the substitution occurs in the para position. These materials are more fully described in U.S. Pat. Ser. No. 706,800 filed Feb. 20, 1968.

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 triarylamines include:

- carboxy radicals;
- hydroxy radicals;
- ethynyl radicals;
- ester radicals (e.g.,



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

- lower alkylene hydroxy radicals (e.g., having one to eight carbon atoms);
- carboxylic acid anhydride radicals;
- lower alkylene carboxy radicals (e.g., having two to eight carbon atoms);

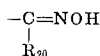
(h) cyano radicals;

(i) acyl halide radicals (e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$  etc.);

(j) amido radicals (e.g.,  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}(\text{R}_{19})_2$  wherein  $R_{19}$  is a

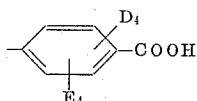
hydrogen atom, an alkyl group or an aryl group);

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

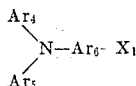


wherein  $R_{20}$  is hydrogen or a lower alkyl radical); l. semicarbazono radicals; and

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



wherein  $D_4$  and  $E_4$  are phenyl or lower alkyl radicals. Photoconductors included in this class can be represented by the following structure:



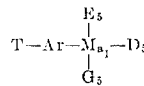
wherein:

- $Ar_4$  and  $Ar_5$  are each a phenyl radical including a substituted phenyl radical such as a halophenyl radical, an alkyl phenyl radical or an amino phenyl radical;
- $Ar_6$  is an arylene radical including a substituted arylene radical such as a phenylene radical or a naphthylene radical; and
- $X_1$  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 methylidene oximido radical or a phenylene carboxy radical. These materials are more fully described in U.S. Pat. Ser. No. 706,780 filed Feb. 20, 1968.

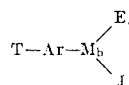
J. Organo-metallic compounds having at least one amino-aryl substituent attached to a Group IVa or Group Va metal atom. The metallic substituents of this class of organic photoconductors are Group IVa or Group Va metals in accordance with the Periodic Table of the Elements (Handbook of Chemistry and Physics, 38th edition, pp. 394-95) and include 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:

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

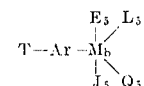
(1)



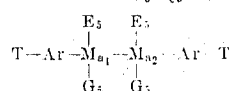
(2)



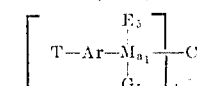
(3)



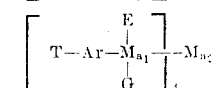
(4)



(5)

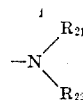


(6)



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

- a hydrogen atom,
- an aryl radical including unsubstituted as well as substituted aryl radicals such as a phenyl radical, naphthyl radical, dialkylaminophenyl radical, or a diarylamino phenyl radical,
- an alkyl radical having one to eight carbon atoms,
- an alkoxy radical having one to eight carbon atoms,
- an aryloxy radical such as phenoxy radical,
- 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

- a heterocyclic radical having 5 to 6 atoms in the hetero nucleus including at least one nitrogen atom such as a triazolyl, a pyridyl radical, etc.; T is an amino radical 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;  $M_{n1}$  and  $M_{n2}$  are the same or different Group IVa metals;  $M_o$  is a Group Va metal;  $D_s$  can be any of the substituents set forth above for  $E_s$ ,  $G_s$ ,  $L_s$  and  $Q_s$  and in addition can be

a Group IVa organometallic radical or when taken with

E, an oxygen atom or a sulfur atom;  $J_s$  can be any of the substituents set forth above for  $E_s$ ,  $G_s$ ,  $L_s$  and  $Q_s$  and in addition can be when taken with E, an oxygen atom or a sulfur atom. These materials are described in U.S. Pat. Ser. No. 650,664 filed July 3, 1967.

K. Any other organic compound which exhibits photoconductive properties such as those set forth in Australia Pat. No. 248,402. Representative organic photoconductors useful in this invention include the compounds listed below;

Table B

diphenylamine	
dinaphthylamine	
N,N'-diphenylbenzidine	
N-phenyl-1-naphthylamine	
N-phenyl-2-naphthylamine	
N,N'-diphenyl-p-phenylenediamine	
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	
N,N,N',N'-tetraphenyl-m-phenylenediamine	
4-acetyltriphenylamine	
4-hexanoyltriphenylamine	
4-lauroyltriphenylamine	
4-hexyltriphenylamine	
4-dodecyltriphenylamine	
4,4'-bis(diphenylamino)benzil	
4,4'-bis(diphenylamino)benzophenone	
poly[N,4''-(N,N',N'-triphenylbenzidine)]	
polyadipyltriphenylamine	
polysebacyltriphenylamine	
polydecamethylenetriphenylamine	
poly-N-(4-vinylphenyl)diphenylamine	
poly-N-(vinylphenyl)- $\alpha$ , $\alpha'$ -dinaphthylamine	
4,4'-benzylidene-bis(N,N-diethyl-m-toluidine)	
4',4''-diamino-4-dimethylamino-2',2''-dimethyltriphenylmethane	
4',4''-bis(diethylamino)-2,6-dichloro-2',2''-dimethyltriphenylmethane	
4',4''-bis(diethylamino)-2',2''-dimethyldiphenylnaphthylmethane	
4',4''bis(dimethylamino-2-chloro-2',2''4',4''-bis(diethylamino)-2-chloro-2',2''-dimethyl-4-dimethylaminotriphenylmethane	
4',4''-bis(diethylamino)-4-dimethylamino-2,2',2''-trimethyltriphenylmethane	
4',4''-bis(dimethylamino)-2-chloro-2',2''-dimethyltriphenylmethane	
4',4''-bis(dimethylamino)-2',2''-dimethyl-4-methoxytriphenylmethane	
Bis(4-diethylamino)-1,1,1-triphenylethane	
Bis(4-diethylamino)tetraphenylmethane	
4',4''-bis(benzylethylamino)-2',2''-dimethyltriphenylmethane	
4',4''-bis(diethylamino)-2',2''-diethoxytriphenylmethane	
4',4'-bis(dimethylamino)-1,1,1-triphenylethane	
1-(4-N,N-dimethylaminophenyl)-1,1,1-diphenylethane	
4-Dimethylaminotetraphenylmethane	
4-Diethylaminotetraphenylmethane	
4,4'-bis(diphenylamino)chalcone	
4-diphenylamino-4'-dimethylaminochalcone	
4-dimethylamino-4'-diphenylaminochalcone	
4,4'-bis(dimethylamino)chalcone	
4,4'-bis(diethylamino)chalcone	
4-diethylamine-4'-diphenylaminochalcone	
4-diphenylaminochalcone	
4'-diphenylaminochalcone	
4'-dimethylaminochalcone	
4'-dimethylaminochalcone	
5 bis-[5-(5H-dibenzo[a,d]cycloheptenyl)]ether	
5-hydroxy-5H-dibenzo[a,d]cycloheptene	
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-dimethylaminonaphthyl)-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- $\beta$ -naphthyl-hydrazine	
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-5hydroxyphenyl)hydrazine	
N,N'-bicarbazyl	
cyclotetrakis(3,9-carbazolylene)	
6-(3-carbazolyl)-cyclotetrakis(3,9-carbazolylene)	
6-(9-carbazolyl)-cyclotetrakis(3,9-carbazolylene)	
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'-bicarbazolyltetra(p-diethylaminophenyl)hydrazine (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-[1-naphthyl]-2-pyrazoline)	
1,5-diphenyl-3-[3'-(1'-p-tolyl-5-phenyl)-2'-pyrazolyl]-2-pyrazoline	
3,3'-bis(1,5-diphenyl-4,5-dimethyl-2-pyrazoline)	
3,3'-bis(1,4,5-triphenyl-2-pyrazoline)	
3,3'-bis(1,5-di-p-tolyl-4-methoxy-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  
 4N,N-bis(p-bromophenyl)aminocinnamic acid  
 1-(4-diphenylamino)naphthacrylic acid  
 p-diphenylaminocinnamic acid  
 p-diphenylaminocinnamonitrile  
 7-diphenylamino coumarin  
 p-diphenylaminophenylvinylacrylic acid  
 p-diphenylaminobenzyl p'-diphenylaminocinnamate  
 7-(p-diphenylaminostyryl)coumarin  
 p-diphenylaminocinnamyl alcohol  
 4-diphenylaminocinnamaldehyde semicarbazone  
 0-p-diphenylaminocinnamoyl p'-diphenylaminobenzaldehyde oxime  
 p-diphenylaminocinnamaldehyde oxime  
 1,3-bis(p-diphenylaminophenyl)-2-propen-1-ol  
 methyl p-diphenylaminobenzoate  
 N,N-diphenylthranilic acid  
 3-p-diphenylaminophenyl-1-1-propanol  
 4-acetyltriphenylamine semicarbazone  
 ethyl 2,6-diphenyl-4-(p-diphenylaminophenyl)benzoate  
 1-(p-diphenylaminophenyl)-1-hydroxy-3-butyne  
 4-hydroxymethyltriphenylamine  
 1-(p-diphenylaminophenyl)ethanol  
 4-hydroxytriphenylamine  
 2-hydroxytriphenylamine  
 4-formyltriphenylamine oxime  
 4-acetyltriphenylamine oxime  
 1-(p-diphenylaminophenyl)hexanol  
 1-(p-diphenylaminophenyl)dodecanol  
 p-diphenylaminobenzoic acid anhydride  
 4-cyanotriphenylamine  
 p-diphenylaminobenzoic acid N,N-diphenylamide  
 p-diphenylaminobenzoic acid  
 p-diphenylaminobenzoyl chloride  
 3-p-diphenylaminophenylpropionic acid  
 4-formyltriphenylamine semicarbazone  
 triphenyl-p-diethylaminophenylsilane  
 methyl-diphenyl-p-diethylaminophenylsilane  
 triphenyl-p-diethylaminophenylgermane  
 triphenyl-p-dimethylaminophenylstannane  
 triphenyl-p-diethylaminophenylstannane  
 diphenyl-di-(p-diethylaminophenyl) stannane  
 triphenyl-p-diethylaminophenylplumbane  
 tetra-p-diethylaminophenylplumbane  
 phenyl-di-(p-diethylaminophenyl)phosphine  
 bis(p-diethylaminophenyl)phosphine oxide  
 tri-p-dimethylaminophenylarsine  
 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  
 methyl-tri-(p-diethylaminophenyl)stannane  
 tetra-p-diethylaminophenylgermane  
 diphenyl-p-diethylaminophenylsilane  
 p-diethylaminophenylarsine  
 tetrakis-[diphenyl-(p-diethylaminophenyl)plumbyl]  
 methane  
 tetrakis-[diphenyl-(p-diethylaminophenyl)stannyl]stannane  
 bis-[phenyl-(p-diethylaminophenyl)]dibismuthine  
 tri-(p-diethylaminophenyl)phosphine sulfide  
 di-(p-diethylaminophenyl)thioxotin

Preferred binders for use in preparing the present photoconductive layers comprise polymers having fairly high dielectric strength which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicon resins; styrene-alkyd resins; silicon-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, polycarbonates; polythiocarbonates; poly(ethylene glycol-co-bishydroxyethoxyphenyl propane terephthalate); etc. Methods of making resins of his 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. No. 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-200 and Lexan 105. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

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

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

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally, 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 as found to be in the range from about 0.002 inch to about 0.006 inch before drying although useful results can be obtained outside of this range.

Suitable supporting materials for coating the photoconductive layers of the present invention can include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity about 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 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, suitable conducting coating can be prepared from the sodium salt of a carboxyester 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 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 low conductivity of the layer in the dark. The electrostatic charge formed on the surface of the photoconductive layer is then selectively dissipated from the surface of the layer by exposure to light through an image-bearing transparency by a conventional exposure operation such as, for example, by contact-printing technique, or by lens projection of an image, etc., to form latent image in the photoconductive 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 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 heating also causes the sensitizing dye to bleach thus rendering the background areas colorless. The heating is generally carried out in temperature range of from about 25° C. to about 150° C. The preferred range is from about 100° C. to about 135° C.

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.

Electrophotographic materials according to the present invention can be applied to reproduction techniques wherein different kinds of radiation i.e., electromagnetic radiations as well as nuclear radiations can be used. For this reason, it is pointed out herein that although materials according to the invention are mainly intended for use in connection with methods comprising an exposure, the term "electrophotography" wherever appearing in the description and the claims, is to be interpreted broadly and understood to comprise both xerography and xeroradiography.

The invention is further illustrated by the following examples which include preferred embodiments thereof.

#### Examples 1-15

Photoconductive compositions containing the sensitizers of the type described herein are separately incorporated into a coating dope having the following composition.

Organic photoconductor 0.25 g.  
Polymeric binder 1.00 g.  
Sensitizer 0.01 g.  
Methylene chloride 9.6 g.

These compositions are then separately coated at a wet thickness of 0.004 inch on a conducting layer comprising the sodium salt of a carboxyester lactone, such as described in U.S. Pat. No. 3,260,706 which in turn is coated on a poly(ethylene terephthalate) film base maintained at 100° F. to provide the coatings described in Table C below. In a darkened room, the surface of each of the photoconductive layers so prepared is either positively or negatively charged to a potential of about 600 volts under a corona charger. The

charged layer is exposed through a stepped density gray scale to the radiation from an incandescent lamp with an illumination intensity of about 75 meter-candles for 12 seconds. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential,  $V_0$ , to some lower potential,  $V$ , whose exact value depends upon the actual amount of exposure received by the area. The element is exposed through each step of the scale and the resultant surface potential measured. The results of these measurements are plotted on a graph of surface potential  $V$  versus log of the exposure for each step. The actual speed of each element is expressed in terms of the reciprocal of the exposure required to reduce the surface potential to any fixed arbitrarily assigned value. The results of these measurements are set forth in the following Table C. The speed is the quotient of  $10^4$  divided by the exposure in meter-candle-seconds required to reduce the potential by 100 volts. The polymeric binder used in the coating compositions is polyester of terephthalic acid and a mixture of ethylene glycol (1 part by weight) and 2,2-bis(4-hydroxyethoxyphenyl)propane (9 parts by weight). The photoconductors referred to in Table C are as follows:

A - Triphenylamine

C - 4,4'-Bis(diethylamino)-2,2'-dimethyltriphenyl methane

G - 4,4'-Bis(diphenylamino)chalcone

TABLE C

Example Number	Sensitizing compound number	Photoconductor	Speed	
			Plus	Minus
1	II	C	320	160
2	V	A	320	160
3	VI	G	630	180
4	IV	G	530	120
5	VII	G	320	180
6	VIII	G	560	160
7	X	A	320	140
8	XI	A	950	630
9	XIII	A	400	1,200
10	XIV	G	320	1,200
11	XV	G	1,000	1,000
12	XVI	G	360	220
13	XVII	G	630	250
14	XVIII	G	500	160
15	XX	G	450	170
			280	500
			450	200
			360	400
			340	320
			340	320
			270	340
			320	200

#### Examples 16 & 17

The procedure of examples 1-15 is repeated except that the sensitizers employed are acridine range and acriflavin both being acridines which are not substituted in both the 9 and 10 positions. The results are set forth in the following Table D.

TABLE D

Example Number	Sensitizing compound	Photoconductor	Speed	
			Plus	Minus
16	Acridine orange	A	32	32
		G	12	6.3
17	Acriflavin	A	50	40
		G	80	10
		G	40	50

Comparing these results with those set forth in examples 1-15, it is seen that substantial increases in speed are attained when compounds are used having substituents in the 9 and 10 positions.

#### Example 18

Coating compositions containing the sensitizing compounds of this invention are prepared and coated in the manner described in examples 1-15. In a darkened room, the surface of each of the photoconductive layers 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  $19 \pm 1$  foot candles. The resulting electrostatic latent image is developed in the usual manner by cascading over the surface of the layer mixture of negatively charged black thermoplastic toner particles on glass beads. A good visible image is produced in each instance.

The sensitizing compounds used in this invention can be prepared by methods similar to those described in the following references:

A. Hantsch Ber. 44 1783; N. S. Drozdov, Trudy Kafedry Biokhim, Moskov. Zootekh. Inst. Konevodstva 1944 48-56 (1945) (C. A. 41 763); Goldberg and Nimerowski [Ber. 40 2448 (1907)]; K. Glewan and A. Schubert [Ber. 73 761 (1940)]; Gomberg, Cone, Ann. 370. 207 (1909); Ullman, Maag, Ber. 40, 2520 (1907); Cone, J. Am. Chem. Soc. 36, 2105 (1914); Gomberg, Tabern, J. Am. Chem. Soc. 48, 1352 (1926); Glen, Schubert Ber. 73. 757 (1940).

A few typical preparations are set forth in the following Examples:

#### Example 19 - Synthesis of N-Phenylacridone

N,N-Diphenylanthranilic acid (25 g., 0.08 moles) is dissolved in 50 ml. of phosphorous oxychloride. The resulting solution is heated on a steam bath for 45 minutes, cooled and then quenched with water. The precipitate which forms is washed with dilute sodium hydroxide solution and recrystallized from 2-methoxyethanol. There is obtained 15 g. (0.055 moles, 69 percent yield) of product m.p. 272-274° C.

#### Example 20 - Synthesis of 9-(4-dimethylaminophenyl)-10-phenyl-9-acridanol (Sensitizer I)

N-Phenylacridone (5.4 g., 0.02 moles) is added to an ether solution of 4-dimethylaminophenyl lithium [prepared from 4-bromo-N,N-dimethylaniline (5.0 g., 0.025 mole) and lithium wire (0.35 g., 0.05 m.) in 25 ml. of dry ethyl ether] and the mixture is stirred and refluxed for 3 hours. Several ml. of water are added to the resulting mixture which turns deep blue for several minutes and then yellow. Filtration and concentration of the ether solution results in the isolation of 5.5 g. (0.014 m., 70 percent yield) of product as colorless crystals, m.p. 147-149° C.

Calculated for $C_{27}H_{24}N_2O$	N, 7.1%
Found	N, 7.5%

#### Example 21 - Synthesis of 9-(4-dimethylaminophenyl)-10-phenyl-acridinium diperchlorate (Sensitizer II)

To a solution of 9-(4-dimethylaminophenyl)-10-phenyl-9-acridanol (1.25 g., 0.0032 m.) in 25 ml. dichloromethane is added concentrated perchloric acid (0.957 g., 0.009 m.). The yellow solid which separates is washed with ether to provide 0.4 g. of product.

Calculated for $C_{27}H_{24}N_2Cl_2O_6$	N, 4.8; Cl, 12.3
Found	N, 4.8; Cl, 12.6

#### Example 22 - Synthesis of 9-(4-dimethylaminophenyl)-10-phenyl-acridinium ditrifluoroacetate (Sensitizer III)

To a solution of 9-(4-dimethylaminophenyl)-10-phenyl-9-acridanol (1.25 g., 0.0032 moles) in 25 ml. of dichloromethane is added trifluoroacetic acid (0.726 g., 0.006 moles). After the solvent is removed the blue-black residue is triturated with ether to provide 0.7 g. of product (m.p. 150-160).

Calculated for $C_{29}H_{23}N_2O_2F_3$	F, 11.7
Calculated for $C_{31}H_{23}N_2O_4F_6$	F, 18.9
Found	F, 16.2

#### Example 23 - Synthesis of 9,10-diphenyl-9-acridanol (Sensitizer IV)

To N-phenylacridone (5.4 g., 0.02 moles) suspended in dry benzene is added phenyl lithium (16 ml.-2M, 0.19 moles) in benzenediethylether. When the resulting mixture is almost entirely in solution it is hydrolyzed with aqueous ammonium chloride. The precipitate which results is extracted with benzene. The benzene solution is dried by azeotroping the water and is concentrated to 100 ml. Hexane is then added to the benzene solution until incipient crystallization occurs. The benzene hexane solution is chilled and 5.8 g. of light yellow crystals (m.p. 178-179) are isolated therefrom.

Calculated for $C_{25}H_{19}NO$	C, 86.0; H, 5.5; N, 4.0
Found	C, 85.8; H, 5.2; N, 3.8

#### Example 24 - Synthesis of 9,10-diphenylacridinium perchlorate (Sensitizer V)

To a solution of 9,10-diphenyl-9-acridanol (0.5 g.) in 10 ml. dichloromethane is added 1 g. of concentrated perchloric acid. The mixture is stirred and the 2.4 g. of yellow solid which separates is isolated and washed with water. The yellow solid is purified by dissolving in a minimum quantity of acetonitrile and adding ethyl ether. The purification step is repeated and a yellow solid obtained.

Calculated for  $C_{25}H_{18}NClO_4$ : C, 69.5; H, 4.2; N, 3.2; Cl, 8.1 Found: C, 69.2; H, 4.2; N, 3.5; Cl, 8.4

#### Example 25 - Synthesis of 9,10-diphenylacridinium ditrifluoroacetate (sensitizer VI)

The procedure used is the same as for the perchlorate except that 0.6 g. of trifluoroacetic acid is added. Crystallization of the crude product from acetonitrile gives yellow crystals which analysis indicates to be a ditrifluoroacetate salt. m.p. 168-170°

Calculated for $C_{29}H_{19}NF_6O_2$	N, 2.5; F, 20.4
Found	N, 3.0; F, 19.9

#### Example 26 - Synthesis of 9,10-Diphenylacridinium fluoroborate (Sensitizer VII)

The procedure of example 24 is used except that fluoroboric acid is employed instead of perchloric. The m.p. is <300°;

$\lambda_{max}^{MeCN} = 265, 362, 430$  ( $\epsilon \times 10^{-4} = 6.10, 1.5, 0.5$ ).  
Calculated for  $C_{25}H_{18}NBF_4$ : C, 71.6; H, 4.3; N, 3.3; B, 2.6; F, 18.2. Found: C, 71.9; H, 4.6; N, 3.3; B, 2.6; F, 17.8.

#### Example 27 - Synthesis of 9,10-Diphenylacridinium hexafluorophosphate (Sensitizer VIII)

A solution consisting of two grams of 9,10-diphenylacridinium perchlorate in 10 ml. dimethylformamide is added by drops to a solution of 2.6 g. of potassium hexafluorophosphate in 75 ml. water. The resulting yellow precipitate is filtered off, washed with water,

$\lambda_{max}^{MeCN} = 265, 365, 435$  ( $\epsilon \times 10^{-4} = 6.50, 1.65, 0.5$ ).  
Calculated for  $C_{24}H_{18}NPF_6$ : C, 62.0; H, 3.9; N, 3.0; P, 6.6; F, 4.5. Found: C, 62.4; H, 3.6; N, 3.1; P, 6.5; F, 4.8.

#### Example 28 - Synthesis of 9-(4-dimethylaminophenyl)-10-phenyl-acridinium chloride (Sensitizer IX)

The procedure used is that described in example 21 except that hydrochloric acid is used instead of perchloric.

#### Example 29 - Synthesis of 9-Pehnyl-10-methylacridinium perchlorate (Sensitizer X)

The procedure used is essentially that described in examples

23 and 24 starting with N-methylacridone (U.S. Pat. No. 2,645,594) instead of N-phenylacridone. The product has a m.p. 210-211 and

shows  $\lambda_{\text{max}}^{\text{MeCN}} = 261, 361 \text{ nm}$  ( $\epsilon \times 10^{-4} = 10.20, 2.10$ ).  
 Calculated for  $\text{C}_{20}\text{H}_{16}\text{NClO}_4$ : C, 65.0; H, 4.4; N, 3.8; Cl, 9.6. Found: C, 64.6; H, 4.5; N, 3.7; Cl, 9.9.

**Example 30 - Synthesis of 9-(4-dimethylaminophenyl)-10-methyl-acridinium iodide (Sensitizer XII)**

The procedure used is essentially that described in following example 33 except that hydriodic acid is used instead of perchloric.

**Example 31 - Synthesis of 9-Phenyl-10-benzylacridinium perchlorate (Sensitizer XIII)**

The procedure used is that described in examples 23 and 24 starting with N-benzylacridone (U.S. Pat. No. 2,645,594) instead

The procedure used is that described in Examples 23 and 24 starting with N-benzylacridone (U.S. Patent 2,645,594) instead of N-phenylacridone. The final product shows  $\lambda_{\text{max}}^{\text{MeCN}} = 262, 362 \text{ nm}$  ( $\epsilon \times 10^{-4} = 9.30, 1.85$ ).

Calculated for  $\text{C}_{26}\text{H}_{20}\text{NClO}_4$ : C, 70.1; H, 4.5; N, 3.1; Cl, 7.9. Found: C, 70.1; H, 4.2; N, 3.0; Cl, 8.1.  
 The intermediate 9-phenyl-10-benzyl-9-acridanol has a M.P. 200° dec. and shows  $\lambda_{\text{max}}^{\text{MeCN}} = 285 \text{ nm}$  ( $\epsilon \times 10^{-4}, 1.60$ ).

Calculated for  $\text{C}_{26}\text{H}_{21}\text{NO}$ : C, 86.0; H, 5.8; N, 3.8. Found: C, 86.1; H, 5.0; N, 4.1.

**Example 32 - Synthesis of 9Phenyl-10benzylacridinium fluoroborate (Sensitizer XIV)**

The procedure used is that described in Example 31 except that fluoroboric acid is used instead of perchloric. The product shows  $\lambda_{\text{max}}^{\text{MeCN}} = 262, 362 \text{ nm}$  ( $\epsilon \times 10^{-4} = 9.40, 1.90$ ).

Calculated for  $\text{C}_{26}\text{H}_{20}\text{NBF}_4$ : N, 3.2. Found: N, 2.9.

**Example 33 - Synthesis of 9-(4-dimethylaminophenyl)-10-methyl-acridinium diperchlorate (Sensitizer XV)**

The procedure used is that referred to in example 29 except that 4-dimethylaminophenyl magnesium bromide is used. The product has m.p. >265°.

Calculated for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Cl}_2\text{O}_8$ : C, 51.5; H, 4.3; N, 5.5; Cl, 13.8. Found: C, 49.8; H, 4.7; N, 5.5; Cl, 14.4.

The intermediate 9-(4-dimethylaminophenyl)-10-methyl-acridanol has M.P. 169°-170° (darkens 150°) and shows  $\lambda_{\text{max}}^{\text{MeCN}} = 255, 275, 380, 398$  ( $\epsilon \times 10^{-4} = 3.80, 2.75, .5, .60$ ).

Calculated for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}$ : C, 80.1; H, 6.7; N, 8.5. Found: C, 79.5; H, 6.4; N, 7.5.

**Example 34 - Synthesis of 9-(4-dimethylaminophenyl)-10-methyl-acridinium difluoroborate (Sensitizer XVI)**

The procedure used is that described in example 33 except that an excess of fluoroboric acid is used instead of perchloric. The resulting product has m.p. >235° Dec. (darkens 190°) and shows

$\lambda_{\text{max}}^{\text{MeCN}} = 261, 361, 380-445$  ( $\epsilon \times 10^{-4} = 7.75, 14.5, 2.5$ ).

Calculated for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{BF}_4$ : C, 52.9; H, 4.4; N, 5.6; B, 4.3; F, 30.5. Found: C, 53.1; H, 4.4; N, 5.0; B, 4.1; F, 29.5.

**Example 35 - Synthesis of 9-(4-dimethylaminophenyl)-10-methyl-acridinium perchlorate (Sensitizer XVII)**

The yellow diperchlorate salt described in Example 33 is washed thoroughly with water and dried. A bronze powder is obtained.

Calculated for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{ClO}_4$ : C, 64.1; H, 5.1; N, 6.8; Cl, 8.5. Found: C, 64.4; H, 5.0; N, 6.8; Cl, 8.9.

**Example 36 - Synthesis of 9-(4-dimethylaminophenyl)-10-methyl-acridinium fluoroborate (Sensitizer XVIII)**

The yellow difluoroborate salt described in example 34 is washed thoroughly with water and dried. A blue powder is obtained.

Calculated for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{BF}_4$ : C, 66.0; H, 5.3; N, 7.0; B, 2.7; F, 19.0. Found: C, 66.0; H, 5.4; N, 6.8; B, 2.7; F, 18.7.

**Example 37 - Synthesis of 9-(4-dimethylaminophenyl)-9-ethoxy-10-benzylacridane (Sensitizer XIX)**

The procedure used is to heat 9-(4-dimethylaminophenyl)-10-benzyl-9-acridanol in ethanol. The product separated on cooling, m.p. = 159-160;  $\lambda_{\text{max}} = 280 \text{ nm}$ . ( $\epsilon \times 10^4 = 2.90$ ).

Calculated for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}$ : C, 83.0; H, 6.9; N, 6.5. Found: C, 82.6; H, 7.0; N, 6.5.

The intermediate 9-(4dimethylaminophenyl)-10-benzyl-9-acridanol is prepared essentially by the procedure described in example 23 by reacting N-benzylacridone with 4-dimethylaminophenyl magnesium bromide. The acridanol has a m.p. 146-148 and shows

$\lambda_{\text{max}}^{\text{MeCN}} = 275 \text{ nm}$  ( $\epsilon \times 10^{-4} = 2.8$ ).

Calculated for  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}$ : C, 82.9; H, 6.4; N, 6.9. Found: C, 83.2; H, 6.3; N, 6.9.

**Example 38 - Synthesis of 9-(4-dimethylaminophenyl)-10-benzyl-acridinium diperchlorate (Sensitizer XX)**

The procedure used is that referred to in example 33 except that N-benzylacridone is used instead of N-methylacridone. The yellow product has m.p. 245-250° Dec.

Calculated for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{Cl}_2\text{O}_8$ : N, 4.8; Cl, 12.1  
 Found: N, 4.6; Cl, 11.8

**Example 39 - Synthesis of 9-(4-dimethylaminophenyl)-10-benzyl-acridinium difluoroborate (Sensitizer XXI)**

The procedure used is that referred to in example 38 except that an excess of fluoroboric acid is used instead of perchloric. The yellow product has a m.p. = 245-250° Dec.

Calculated for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{BF}_4$ : N, 5.0  
 Found: N, 4.9

**Example 40 - Synthesis of 9-(4-dimethylaminophenyl)-10-benzyl acridinium perchlorate (Sensitizer XII)**

The diperchlorate salt described in example 38 is washed thoroughly with water and dried. A blue product is obtained.

Calculated for  $\text{C}_{32}\text{H}_{31}\text{N}_2\text{ClO}_4$ : N, 5.7; Cl, 7.2  
 Found: N, 5.5; Cl, 7.6

**Example 41 - Synthesis of 9-(4-dimethylaminophenyl)-10-benzyl acridinium fluoroborate (Sensitizer XXIII)**

The difluoroborate salt described in example 39 is washed thoroughly with water and dried. A blue product is obtained.

Calculated for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{BF}_4$ : C, 70.6; H, 5.3; N, 5.9; B, 2.3; F, 16.0. Found: C, 70.1; H, 5.1; N, 5.9; B, 2.2; F, 16.4.

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:

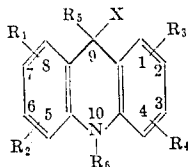
1. An electrophotographic element comprising a support having coated thereon a layer of a photoconductive composition comprising a photoconductor and a sensitizer which is a

9,10-substituted acridine, wherein the 9 and 10 substituents on the acridine nucleus are each selected from the group consisting of an alkyl group and an aryl group.

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

3. The element of claim 1 wherein the photoconductive composition contains 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 having the structure:



wherein:

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each selected from the group consisting of hydrogen, an alkyl group, an amino group, a halogen atom, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, a nitro group, a hydroxy group, a cyano group and an acyl group;

R<sub>5</sub> and R<sub>6</sub> are each selected from the group consisting of an alkyl group and an aryl group; and

X represents a substituent which is dissociated to some extent as an anion.

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 9,10-diphenylacridinium perchlorate.

7. An electrophotographic element comprising a support having coated thereon a layer of 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

9,10-diphenylacridinium ditrifluoroacetate.

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

- a. about 10 percent to 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 9,10-diphenylacridinium fluoroborate.

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

- a. about 10 percent to 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 9,10-diphenylacridinium hexafluorophosphate.

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

- a. about 10 percent to 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 9-phenyl-10-methylacridinium perchlorate.

11. A photoconductive composition comprising a photoconductor and a sensitizer which is a 9,10-substituted acridine, wherein the 9 and 10 substituents on the acridine nucleus are each selected from the group consisting of an alkyl group and an aryl group.

12. The composition of claim 11 wherein the photoconductor is an organic photoconductor.

13. The composition of claim 11 including a polymeric film-forming binder.

14. In an electrophotographic process wherein an electrostatic charge pattern is formed on a photoconductive element, the improvement characterized in that said photoconductive element has a photoconductive layer comprising an organic photoconductor and a 9,10-substituted acridine as a sensitizer, wherein the 9 and 10 substituents on the acridine nucleus are each selected from the group consisting of an alkyl group and an aryl group.

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