3,560,209 Patented Feb. 2, 1971

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3,560,209

ELECTROPHOTOGRAPHIC SENSITIZING DYES Philip W. Jenkins, Donald W. Heselfine, and John D. Mee, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y. No Drawing. Filed Oct. 9, 1968, Ser. No. 766,327 Int. Cl. G03g 5/06 US Cl. 96-16 46 Claims

U.S. Cl. 96-1.6

ABSTRACT OF THE DISCLOSURE

Compounds containing a heterocyclic nitrogen atom substituted by an -OR group are useful as sensitizers for photoconductors in electrophotographic elements. 15

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

20The process of xerography, as disclosed by Carlson in U.S. 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 25receives 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 30 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 con-35 tacting 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 in the absence of charge 40pattern as desired. The deposited marking material can then be either permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor, or the like, or transferred to a second element to which it may similarly be fixed. Likewise, the 45 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 50 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 55 many organic compounds have also been screned 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 60 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 trans- 65 parent 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 70 images has been removed by transfer and/or cleaning.

Although some of the organic photoconductors com-

2

prising 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 regions of the spectrum has several advantages: it makes available inexpensive and convenient light sources such 10 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 other-

wise 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 a novel class of sensitizers for use in combination with

photoconducting compounds so that reproductions are obtainable.

Another object of this invention is to provide novel sensitized photoconductive elements.

It is also an object to provide novel sensitized photoconductive compositions which can be positively and negatively charged.

These and other objects of this invention are accomplished with photoconductive compositions sensitized with compounds having one of the following structures:

$$\begin{array}{c} \left\langle \begin{array}{c} Z \\ N \end{array} \right\rangle \\ \left\langle \begin{array}{c} X \\ N \end{array} \\ \left\langle \begin{array}{c} X \\ N \end{array} \right\rangle \\ \left\langle \begin{array}{c} X \\ N \end{array} \right\right\rangle \\ \left\langle \begin{array}{c} X \\ \\ \left\langle \end{array} \right\rangle \\ \left\langle \begin{array}{c} X \\ \\ \\ \left\langle \end{array} \right\rangle \\ \right\rangle$$
 \\ \left\langle \begin{array}{c} X \\ \\ \\ \left\langle \end{array} \right\rangle \\ \left\langle \end{array} \right\rangle \right\right\rangle

wherein:

etc .:

R₁ represents a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes, e.g., those set forth in Mees and James, The Theory Of The Photographic Process, MacMillan 3rd ed., pp. 198-232; the methine linkage can be substituted or unsubstituted, e.g., $-CH =, -(CH_3) =, -C(C_6H_5) =,$

 R_8 represents a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes, e.g., those in the above reference or an allylidene radical including a substituted allylidene radical such as a cyanoallylidene radical, an alkoxycarbonylallylidene radical or an alkylsulfonylallylidene radical; the methine linkage can be substituted or unsubstituted;

R represents either:

(a) an alkyl radical preferably having 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl, etc., including substituted alkyl radicals such as sulfoalkyl, e.g., $(CH_2)_3SO_3$, an aralkyl, e.g., benzyl or pyridinato-oxy-alkyl salt, e.g., $-(CH_2)_3$ -O-Y wherein Y is a substituted or unsubstituted pyridinium salt;

(b) an acyl radical, e.g.,

 $-C-R_4$ Ĭ

wherein R₄ is an alkyl radical preferably having 1 to 8 carbon atoms e.g., methyl, ethyl, propyl, butyl, phenyl, naphthyl, etc.;

(c) an aryl radical including a substituted aryl radical e.g., phenyl, naphthyl, tolyl, etc.;

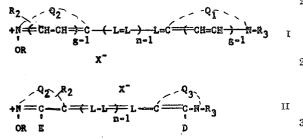
Z represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus including a substituted heterocyclic nucleus which nucleus can contain at least one additional hetero atom such as oxygen, sulfur, selenium or nitrogen, e.g., a pyridine nucleus, an indole nucleus, a quinoline nucleus, etc.; and

X- represents an acid anion.

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The preferred sensitizers of this invention have a first and a second 5 to 6 membered nitrogen-containing heterocyclic nucleus joined by a methine linkage. The first of these nuclei can be either (1) a 1-alkoxy-2-aryl-indole nucleus joined at the 3-carbon atom thereof to the methine linkage; (2) a 1-alkoxypyridine nucleus joined at the 2-carbon atom thereof to the methine linkage. The second nucleus is a desensitizing nucleus (as defined infra) joined at a carbon atom thereof to the methine linkage if the first nucleus is an arylindole as described under (1). The second nucleus can also be a heterocyclic nucleus of the type contained in cyanine dyes joined at a carbon atom to the methine linkage if the first nucleus is a pyridine or quinoline as described in (2) or (3) above. The methine linkage preferably contains from 2 to 3 carbon atoms in the chain, i.e., a dimethine linkage, or a trimethine linkage which may also contain at least one side chain group.

The preferred class of sensitizing dyes of this invention include those defined by the following formulae:



wherein Q_1 , Q_2 , Q_3 and Q_7 each represent the non-metallic atoms necessary to complete a sensitizing or desensitizing nucleus containing from 5 to 6 atoms in the heterocyclic ring, which nucleus may contain a second hetero atom such as oxygen, sulfur, selenium or nitrogen, i.e., a nucleus of the type used in the production of cyanine dyes, such as the following representative nuclei: A thiazole nucleus, e.g., thiazole, 4-methylthiazole, 3-ethylthiazole, 45 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4- or 5-nitrobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-50 methylbenzothiazole, 6-methylbenzothiazole, 6-nitrobenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-chloro-6-nitrobenzothiazole, 4-phenylbenzothiazole, 4methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothia- 55 zole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5-6 - dimethoxybenzothiazole, 5,6methylenedioxybenzothiazole, 5-hydroxybenzothiazole, 6hydroxybenzothiazole, α -naphthothiazole, β -naphthothiazole, β , β -naphthothiazole, 5-methoxy- β , β -naphthothiazole, 5-ethoxy- β -naphthothiazole, 8-methoxy - α - naphthothiazole, 7-methoxy- α -naphthothiazole, 4'-methoxythianaphtheno-7',6',4,5-thiazole, nitro group substituted naphthothiazoles, etc.; an oxazole nucleus, e.g., 4-methyloxazole, 4-nitro-oxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-di-65 phenyloxazole, 4 - ethyloxazole, 4,5 - dimethylazole, 5-phenyloxazole, benzoxazole, 5 - chlorobenzoxazole, 5 - methylbenzoxazole, 5 - phenylbenzoxazole, 5 - or 6-nitrobenzoxazole, 5 - chloro - 6 - nitrobenzoxazole, 6 -methylbenzoxazole, 5,6 - dimethylbenzoaxazole, 4,6 - 70 dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, α naphthoxazole, β -naphthoxazole, nitro group substituted

selenazole, 4-nitroselenazole, 4-phenylselenazole, benzoselenazole, 5 - chlorobenzoselenazole, 5 - methoxybenzoselenazole, 5 - hydroxybenzoselenazole, 5- or 6-nitrobenzoselenazole, 5-chloro-6-nitrobenzoselenazole, tetrahydrobenzoselenazole, α -naphthoselenazole, β -naphthoselenazole, nitro group substituted naphthoselenazoles, etc.; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, 4-nitrothiazoline, etc.; a pyridine nucleus, e.g., a 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4pyridine, nitro group substituted pyridines, etc.; a quino-

10 line nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 6-nitro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 6-nitro-4-quinoline, 7-methyl-4-

quinoline, 8-chloro-4-quinoline, 1-isoquinoline, 6-nitro-1isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc.; a 3,3-dialkylindolenine nucleus, preferably having a nitro or cyano substituent, e.g., 3,3-dimethyl-5 or 6-nitro-

20 indolenine, 3,3-dimethyl-5- or 6-cyanoindolenine, etc.; and, an imidazole nucleus e.g., imidazole, 1-alkylimidazole. 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, benzimidazole, 1-alkylbenzimidazole, 1-alkyl-

5 - nitrobenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 25 1-alkyl- α -naphthimidazole, 1-aryl- β -naphthimidazole, 1alkyl-5-methoxy- α -naphthimidazole, or an imidazo [4,5-b]quinoxaline nucleus, e.g., 1-alkylimidazo[4,5-b]quinoxaline such as 1-ethylimidazo[4,5-b]quinoxaline such as 1ethylimidazo[4,5-b]quinoxaline, 6-chloro-1-ethylimidazo-30 [4,5-b]quinoxaline; etc., 1 - alkenylimidazo[4,5-b]quin-oxaline such as 1-allylimidazo[4,5-b]quinoxaline, 6-chloro-1 - allylimidazo[4,5-b]quinoxaline, etc., 1 - arylimidazo [4,5-b]quinoxaline such as 1-phenylimidazo[4,5-b]quinoxaline, 6-chloro-1-phenylimidazo[4,5-b]quinoxaline, etc.; 35 a 3,3-dialkyl-3H-pyrrolo[2,3-b]pyridine nucleus e.g., 3,3dimethyl - 3H - pyrrolo[2,3-b]pyridine, 3,3-diethyl-3-Hpyrrolo[2,3-b]pyridine, etc.; a thiazolo[4,5-b]quinoline nucleus; an indolyl nucleus including substituted indolyl nuclei such as a 2-phenyl-3-indole, 1-methyl-2-phenyl-3-40 indole; and the like; R represents either (1) an alkyl radical including a substituted alkyl (preferably a lower alkyl having 1 to 4 carbon atoms) e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, alkaryl such as benzyl, sulfoalkyl such as β -sulfoethyl, ω -sulfobutyl, ω -sulfopropyl, or (2) an acyl radical, e.g.,

wherein R_6 is an alkyl including a substituted alkyl or an aryl such as naphthyl, phenyl, methyl, propyl, benzyl, etc.; n is a positive integer from 1 to 4; m is a positive integer from 1 to 3; g is a positive integer from 1 to 2; L represents a methine linkage, e.g. -CH=, $-C(CH_3)=$, $-C(C_6H_5)=$, etc.; D, E, J and R₂ each represent a hydrogen atom, an alkyl group (preferably a lower alkyl containing from 1 to 4 carbon atoms) e.g., methyl, ethyl, propyl, isopropyl, butyl, decyl, dodecyl, etc. or an aryl group, e.g., phenyl, tolyl, naphthyl, meth-oxyphenyl, chlorophenyl, nitrophenyl, etc.; X represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, tetrafluoroborate, sulfamate, thiocyanate, p-toluenesulfonate, methyl sulfate, etc.; R_3 represents an alkyl group, including substituted alkyl, (preferably a lower alkyl containing from 1 to 4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups, (preferably a substituted lower alkyl containing from 1 to 4 carbon atoms), such as a hydroxyalkyl group, e.g., β -hydroxyethyl, ω -hydroxybutyl, etc., an alkoxyalkyl group, e.g., β -methoxyethyl, ω butoxybutyl, etc., a carboxyalkyl group, e.g., β -carboxyethyl, ω -carboxybutyl, etc., a sulfoalkyl group, e.g., β sulfoethyl, ω-sulfobutyl, etc., a sulfatoalkyl group, e.g., β -sulfatoethyl, ω -sulfatobutyl, etc., an acyloxyalkyl group, e.g., β -acetoxyethyl, γ -acetoxypropyl, ω -butyryloxybutyl, naphthoxazoles, etc.; a selenazole nucleus, e.g., 4-methyl- 75 etc., an alkoxycarbonylalkyl group, e.g., β -methoxycar-

bonylethyl, ω -ethoxycarbonylbutyl, etc. or an aralkyl group, e.g., benzyl, phenethyl, etc.; an alkenyl group, e.g., allyl, 1-propenyl, 2-butenyl, etc., or an aryl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc. In the above formulae Q_2 is preferably a pyridine, indole or quinoline nucleus. Also D, E and J are preferably aryl radicals. Nuclei wherein Q1, Q2, Q3 and Q7 complete an imidazo [4,5-b]quinoxaline nucleus, or a nitro group substituted thiazole, oxazole, selenazole, thiazoline, pyridine, quinoline, indole, or imidazole nucleus are de-10 sensitizing nuclei.

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

those organic compounds which exhibit an electrophotosensitivity to light and are capable of forming substantially transparent elements when coated on transparent film bases. An especially useful class of organic photoconductors is referred to herein as "organic amine" photoconductors. Such organic photoconductors have as a common structural feature at least one amino group. Useful organic photoconductors which can be spectrally sensitized in accordance with this invention include, therefore, arlyamine compounds comprising (1) diarylamines such as 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-anilinophe-

1 3-ethyl-1'-methoxyoxa-2'-pyridocarbocyanine perchlorate.
2 1'-ethoxy-3-ethyloxa-2'-pyridocarbocyanine tetrafluoroborate.
3 3'-ethyl-1-methoxy-2-pyridocarbocyanine iodide.
4 1-ethoxy-3'-ethyl-2-pyridothiacyanine tetrafluoroborate.
5 1-benzyloxy-3'-ethyl-2-pyridothiacyanine iodide.
6 3'-ethyl-1-methoxy-2-pyridothiacarbocyanine iodide.
71-ethoxy-3'-ethyl-2-pyridothiacarbocyanine tetrafluoroborate.
8 Anhydro-3'-ethyl-1-(3-sulfopropoxy)-2-pyridothiacarbocyanine hydroxide.
9 1-benzyloxy-3'-ethyl-2-pyridothiacarbocyanineperchlorate.
103'-ethyl-1-methoxy-2-pyridothiadicarbocyanineperchlorate.
111'-methoxy-1,3,3-trimethylindo-2'-pyridocarbocyaninepicrate.
12 3'-ethyl-1-methoxy-4',5'-benzo-2-pyridothiacarbocyanineperchlorate.
131-ethoxy-3'-ethyl-4',5'-benzo-2-pyridothiacarbocyaninetetrafluoroborate.
14
151'-ethoxy-3-ethylthia-2'-cyanine tetrafluoroborate.
161'-ethoxy-3-ethylthia-2'-carbocyanine tetrafluoroborate.
17 1'-ethoxy-3-ethylthia-2'-dicarbocyanine tetrafluoroborate.
181-methoxy-3'-methyl-2-pyridothiazolinocarbocyanine perchlorate.
193'-ethyl-1-methoxy-4-pyridothiacyanine perchlorate.
203'-ethyl-1-methoxy-4-pyridothiacarbocyanine perchlorate.
211,1'-dimethoxy-2,2'-diphenyl-3,3'-indolocar bocyanine perchlorate.
22 1-methoxy-1'-methyl-2,2',10-triphenyl-3,3'-indolocarbocyanine perchlorate.
231,1'-diethoxy-2,2'-diphenyl-3,3'-indolocarbocyanine perchlorate.
241-ethoxy-1'-methyl-2,2',10-triphenyl-3,3'-indolocarbocyanine perchlorate.
251'-ethoxy-3-ethyl-4,5-benzothia-2'-carbocyanine tetrafluoroborate.
26 1-ethyl-1'-methoxy-4,5-benzothia-4'-carbocyanine perchlorate.
27 3'-ethyl-1-methoxy-6'-nitro-2-phenyl-3-indolothiacarbocyanine p-toluenesulfonate.
281-ethoxy-3'-ethyl-6'-nitro-2-phenyl-3-indolothiacarbocyanine p-toluenesulfonate.
29 1,3-diallyl-1'-methoxy-2'-phenylimidazo[4,5-b]-quinoxalino-3'-indolocarbocyanine perchlorate.
301,3-diallyl-1'-ethoxy-2'-phenylimidazo[4,5-b]-quinoxalino-3'-indolocarbocyanine perchlorate.
31 1'-methoxy-1,3,3-trimethyl-5-nitro-2'-phenylindo-3'-indolocarbocyanine perchlorate.
321-methoxy-1',3',3'-trimethyl-2-phenyl-3-indolo-2'-pyrrolo[2,3-b]pyridocarbocyanine perchlorate.
33 1'-ethoxy-1,3,3-trimethyl-5-nitro-2'-phenylindo-3'-indolocarbocyanine-p-toluenesulfonate.
341-ethoxy-1',3',3'-trimethyl-2-phenyl-3-indolopyrrolo[2,3-b]pyridocarbocyanine perchlorate.
351-acetoxy-2-(4-dimethylaminostyryl)pyridinium perchlorate.
361-benzoyloxy-2-(4-dimethylaminostyryl)pyridinium perchlorate.
37 1.3-diethyl-5-[(1-methoxy-2(1H)-pyridylidene)ethylidene]-2-thiobarbituric acid.
38 3-ethyl-5-[(1-methoxy-2(1H)-pyridylidene)ethylidene]-rhodanine.
39 1,3-diethyl-5-((1-methoxy-2(1H)-pyridylidene)ethylidene]-barbituric acid.
40
41 3-cyano-5-[(1-methóxy-2(1Ĥ)-pyridylidene)ethylidene]-4-phenyl-2(5Ĥ)-furanone.

TABLE A

The preparations of the sensitizing compounds used in this invention are described in copending application Ser. 45 No. 766,307 of Jenkins, Heseltine and Mee titled "Energy-Sensitive Systems" filed Oct. 9, 1968.

Electrophotographic elements of the invention can be prepared with a wide variety of organic photoconductive compounds and the described sensitizing compounds in 50 the usual manner, i.e., by blending a dispersion or solution of the photo-conductive compound together with a binder, when necessary or desirable, and coating or forming a layer with the photoconductive composition. Generally, a suitable amount of the sensitizing compound 55 is mixed with the photoconductive coating composition so that, after thorough mixing, the sensitizing compound is substantially uniformly distributed throughout the desired layer of the coated element. The amount of sensitizer that can be added to a photoconductor-incorporat- 60 ing 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 65 at a concentration of at least about 0.0001 percent and generally in the range from about 0.0001 to about 30 percent by weight based on the weight of the film-forming coating composition. Normally, a sensitizer is added to the coating composition in an amount from about 70 0.005 to about 5.0 percent by weight of the total coating composition.

The sensitizers of this invention are effective for enhancing the electrophotosensitivity of a wide variety of photoconductors. The preferred photoconductors are 75

nol; N,N'-di-2-naphthyl-p-phenylenediamine; those described in Fox U.S. Pat. 3,240,597 issued Mar. 15, 1966, and the like, and (2) triarylamines including (a) nonpolymeric triarylamines, such as triphenylamine, N,N, \hat{N}' , \hat{N}' -tetraphenyl-m-phenylenediamine; 4-acetyltriphenyl-amine, 4 - hexanoyltriphenylamine; 4-lauroyltriphenylamine; 4-hexyltriphenylamine, 4-dodecyltriphenylamine, 4,4'-bis(diphenylamino)benzyl, 4,4'-bis(diphenylamino)benzophenone, and the like, and (b) polymeric triarylamines such as poly[N,4"-(N'N',N'-triphenylbenzidine)]; polyadipyltriphenylamine, polysebacyltriphenylamine: polydecamethylenetriphenylamine; poly-N-(4vinylphenyl)diphenylamine, poly - N-(vinylphenyl)- α , α' dinaphthylamine and the like. Other useful amine-type photoconductors are disclosed in U.S. Pat. 3,180,730 issued Apr. 27, 1965. In addition, photoconductive substances capable of being spectrally sensitized in accordance with this invention are disclosed in Fox U.S. Pat. 3,265,496 issued Aug. 9, 1966, and include those represented by the following general formula:

$$\begin{bmatrix} \mathbf{N} - \mathbf{A} - \\ \mathbf{A}' \end{bmatrix}_{\mathbf{b}}^{\mathbf{Q}}$$

G-

wherein A 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 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc.), an alkoxy group having from 1 to about 6

3,560,209

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carbon atoms (e.g., methoxy, ethoxy, propoxy, pentoxy, etc.), or a nitro group; A' represents a mononuclear 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 1 to about 6 carbon atoms (e.g., acetyl, propionyl, butyryl, etc.), an alkyl group having from 1 to together the necessary atoms to form a heterocyclic amino group typically having 5 to 6 atoms in the ring such as morpholino, pyridyl, pyrryl, etc. At least one of D, E, and M is preferably p-dialkylaminophenyl group. When J is an alkyl group, such an alkyl group more generally has 1 to 7 carbon atoms.

Representative useful polyarylalkane photoconductors include the compounds listed below:

TABLE B

about 6 carbon atoms (e.g., methyl, ethyl, propyl, butyl, etc), an alkoxy group having from 1 to about 6 carbon atoms (e.g., methoxy, propoxy, pentoxy, etc.), or a nitro group; Q can represent a hydrogen atom, a halogen atom or an aromatic amino group, such as A'NH—; b represents an integer from 1 to about 12, and G 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.

Polyarylalkane photoconductors are particularly useful in producing the present invention. Such photoconductors are described in U.S. Pat. 3,274,000; French Pat. 1,383,461 and in copending application of Seus and Goldman entitled "Photoconductive Elements Containing Organic Photoconductors" filed Apr. 3, 1967. These photoconductors include leuco bases of diaryl or triarylmethane 45dye salts, 1,1,1-triarylalkanes wherein the alkane moiety has at least two carbon atoms and tetraarylmethanes, there being substituted an amine group on at least one of the aryl groups attached to the alkane and methane moieties of the latter two classes of photoconductors 50which are non-leuco base materials.

Preferred polyaryl alkane photoconductors can be represented by the formula:

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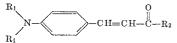
wherein each of D, E and M is an aryl group and J is a hydrogen atom, an alkyl group, or an aryl group, at least one of D, E and M containing an amino substituent. 60 The aryl group attached to the central carbon atom are preferably phenyl groups, although naphthyl groups can also be used. Such aryl groups can contain such substituents as alkyl and alkoxy typically having 1 to 8 carbon atoms, hydroxy, halogen, etc. in the ortho, meta or 65para 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 L can be an alkyl group typically having 1

Additional organic photoconductors which can be employed with the sensitizing compounds described herein are non-ionic cycloheptenyl compounds such as those described in copending application Ser. No. 654,091, filed July 18, 1967; the N,N-bicarbazyls and tetra-substituted 30 hydrazines; the 3,3'-bis-1,5-diarylpyrazolines; triarylamines having at least one of the aryl radicals substituted by either a vinyl radical, or a vinylene radical having at least one active hydrogen-containing group such 35 as p-diphenylaminocinnamic acid; triarylamines substituted by an active hydrogen-containing group, e.g., 4carboxytriphenylamine; and those described in Australian Pat. 248,402. Other organic photoconductors that can be sensitized in accordance with the invention include organometallic compounds which are the organic derivatives of 40 Group IVa and Va metals such as those having at least one aminoaryl group attached to the metal atom as described in Ser. No. 650,664 filed July 3, 1967. Exemplary organo-metallic compounds are the triphenyl-p-dialkylaminophenyl derivatives of silicon, germanium, tin and lead and the tri-p-dialkylaminophenyl derivatives of arsenic, antimony, phosphorous and bismuth.

Another class of photoconductors useful in this invention are the 4-diarylamino-substituted chalcones. Typical compounds of this type are low molecular weight nonpolymeric ketones having the general formula:



wherein R1 and R2 are each phenyl radicals including substituted phenyl radicals and particularly when R₂ is a phenyl radical having the formula:



where R₃ and R₄ are each aryl radicals, aliphatic residues of 1 to 12 carbon atoms such as alkyl radicals preferably having 1 to 4 carbon atoms or hydrogen. Particularly advantageous results are obtained when R₁ is a phenyl radical including substituted phenyl radicals and where R_2 is diphenylaminophenyl, dimethylaminophenyl, or phenyl.

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; silicone resins; styreneto 8 carbon atoms, a hydrogen atom, an aryl group, or 75 alkyd resins; silicone-alkyd resins; soya-alkyd resins; poly-

(vinyl chloride); poly(vinylidene chloride); vinylidene chloride-acrylonitrile copolymers; poly(vinylacetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly-(n-butylmethacrylate), poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylenealkaryloxyalkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamides; polycarbonate; polythiocarbonates; poly(ethylenglycol-co-bishydroxyethoxyphenyl propane terephthalate); nuclear substituted polyvinyl haloarylates; etc. Methods of making resins of this type have been described in the prior art, for example, styrenealkyd resins can be prepared according to the method 15 described in U.S. Pats. 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 at Vitel PE-101, Cymac, Piccopale 100, Saran F-220 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, 2-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 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 $_{45}$ 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 out- 50 side 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 above 20 percent); 55 aluminum-paper laminates; metal foils such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass, and galvanized plates; vapor deposited metal layers such as silver, nickel, aluminum and the like coated on paper or conventional photographic film bases. 60 An especially useful conducting support can be prepared by coating a transparent film support material such as poly(ethylene terephthalate), cellulose acetate, polystyrene, etc., with a layer containing a semiconductor such as cuprous iodide dispersed or imbibed in a resin. Such 65 conducting layers both with and without insulating barrier layers are described in U.S. Pat. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone of maleic anhydride and a vinyl acetate polymer. Such kinds of con- 70 ducting layers and methods for their optimum preparation and use are disclosed in U.S. 3.007,901 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 75 tion from a 60 watt incandescent lamp at a distance of

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 low 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 latent image in the photoconducting layer. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that light causes the charge to be conducted away in pro-

portion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then developer may be used in which the developing particles 20 dium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust, e.g., pow-

der, a pignment in a resinous carrier, i.e., toner, or liquid developed 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. 2,297,691 and in Australian 30 Pat. 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 ad-35 here 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 40 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 radiations, i.e., electromagnetic radiations as well as nuclear radiations, can be used. For this reasons, 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 following examples are included for a further understanding of the invention.

EXAMPLES 1-13

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

Organic photoconductor-0.15 g. Polymeric binder-0.50 g.

Sensitizer-0.002 g.

Methylene chloride or tetrahydrofuran-5 ml.

These composition are then separately coated at a wet thickness of 0.004 inch on an aluminum surface 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 radia $\mathbf{5}$

10

wherein:

100 cm. which provides an illumination intensity of about 75 meter-candles. The exposure causes reduction of the surface potential of the element under each step of the gray scale from its initial potential, Vo, 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 15 meter-candle-seconds required to reduce the potential by 100 volts. The polymeric binder used in the coating compositions is a 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 20 photoconductors referred to in Table C are as follows:

-Triphenylamine

B-4,4'-bis(diethylamino)-2,2'dimethyltriphenyl methane

	Sensitizing compound No.*	Dhata	Speed	
		Photo- — conductor	Plus	Minus
Example No.:				
1	21	A	1,900	1,800
2	21	B	1,600	700
3	22	A	2,100	1,600
4	22	B	1,800	1,800
5	27	Α	´800	1,000
6	27	B	1,200	630
7	29	Ā	1,100	1,100
8	29	B	1,400	1,000
9	31	Δ	1,300	900
10	31	B	1,000	500
11	32		1,100	900
		A		800
12	32	B	1,000	
13	None	A	5	5
		B	5	5

*See Table A.

The above data establish that the dyes of this invention provide substantial increases in speed of organic photoconductors.

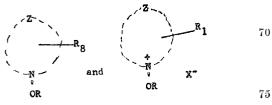
EXAMPLE 14

Coating compositions containing the sensitizing com- 45 pounds of this invention are prepared and coated in the manner described in Examples 1-13. 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 50 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+1 foot candles. The resulting electro-static latent image is developed in the usual manner by cascading 55 over the surface of the layer a mixture of negatively charged black thermoplastic toner particles on glass beads.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and 60 modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photoconductive composition comprising an or- 65 ganic photoconductor and a sensitizer having a formula selected from the group consisting of:



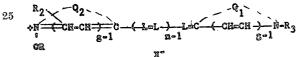
12

- R_1 is a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes;
- R_8 is selected from the group consisting of a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes and an allylidene radical:
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- X is an acid anion and
- Z represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus.

2. The photoconductive composition of claim 1 wherein Z represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

3. The photoconductive composition of claim 1 wherein R_1 is a methine linkage terminated by a 5 to 6 membered heterocyclic nucleus having at least one hetero nitrogen atom.

4. A photoconductive composition comprising an organic photoconductor and a sensitizer having the formula:

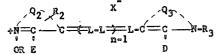


 $_0$ wherein:

- Q1 and Q2 each represent the non-metallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus;
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R_2 is selected from the group consisting of an aryl radical, a hydrogen atom and an alkyl radical;
- R_3 is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methine linkage;
- X is an acid anion;
- g is a positive integer from 1 to 2; and
- n is a positive integer from 1 to 4.

5. The photoconductive composition of claim 4 wherein Q_2 represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

6. A photoconductive composition comprising an organic photoconductor and a sensitizer having the formula:



wherein:

- Q_2 and Q_3 each represent the non-metallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus:
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R_2 , D and E are each selected from the group consisting of an aryl radical, a hydrogen atom and an alkyl radical:
- R₃ is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methine linkage;
- X is an acid anion; and
- n is a positive integer from 1 to 4.

7. The photoconductive composition of claim 6 wherein Q_2 represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus. 75 a quinoline nucleus and an indole nucleus.

20

8. A photoconductive composition comprising an organic photoconductor and a sensitizer having the formula:

wherein:

- Q2 and Q7 each represent the non-metallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus:
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R_2 and J are each selected from the group consisting of an aryl radical, a hydrogen atom and an alkyl 15 radical:
- R₃ is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methine linkage;
- X is an acid anion;
- m is a positive integer from 1 to 3; and
- g is a positive integer from 1 to 2.

9. The photoconductive composition of claim 8 wherein Q2 represents the atoms necessary to complete a mem-25ber selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

10. A photoconductive composition comprising an organic photoconductor and a cyanine dye sensitizer having a first and a second 5 to 6 membered nitrogen-containing heterocyclic nucleus joined by a methine linkage; the first of said nuclei being a 1-alkoxy-2-arylindole nucleus joined at the 3-carbon atom thereof to said linkage; and said second nucleus being a desensitizing nucleus joined

20. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising an organic photoconductor and a sensitizer having a formula selected from the group consisting of:

$$\begin{pmatrix} \mathbf{Z}_{\mathbf{N}} \\ \mathbf{N}_{\mathbf{N}} \end{pmatrix} = \mathbf{R}_{\mathbf{S}} \text{ and } \begin{pmatrix} \mathbf{Z}_{\mathbf{N}} \\ \mathbf{N}_{\mathbf{N}} \end{pmatrix} = \mathbf{R}_{\mathbf{N}} \\ \mathbf{O}_{\mathbf{R}} \\ \mathbf{O}_{\mathbf{R}} \end{pmatrix} = \mathbf{C}_{\mathbf{N}} \mathbf{C}_{\mathbf{N}}$$

10 wherein:

- R_1 is a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes;
- R_8 is selected from the group consisting of a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes and an allylidene radical;
- R is selected from the group consisting of an alkyl radical and an acyl radical,
- X is an acid anion and
- Z represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus.

21. The electrophotographic element of claim 20 wherein Z represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

22. The electrophotographic element of claim 20 wherein R_1 is a methine linkage terminated by a 5 to 6 membered heterocyclic nucleus having at least one hetero nitrogen atom. 30

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

$$\begin{array}{c} R_2 \\ \downarrow \\ \uparrow \\ \downarrow \\ CH \\ CH \\ GR \\ g=1 \\ \hline \\ GR \\ \downarrow \\ g=1 \\ \hline g=1$$

at a carbon atom thereof to said linkage, to complete said cyanine dye sensitizer.

11. A photoconductive composition in accordance with claim 10 wherein said cyanine dye sensitizer contains a 2-aryl-indole desensitizing nucleus.

4512. A photoconductor composition in accordance with claim 10 wherein said cyanine dye sensitizer contains an imidazo[4,5-b]quinoxaline desensitizing nucleus.

13. A photoconductive composition in accordance with claim 10 wherein said cyanine dye sensitizer contains a $_{50}$ nitro substituted desensitizing nucleus.

14. A photoconductive composition in accordance with claim 13 wherein said cyanine dye sensitizer contains a 6-nitrobenzothiazole desensitizing nucleus.

15. A photoconductive composition in accordance with 55claim 13 wherein said desensitizing nucleus is a 5-nitro-2phenyl indole nucleus.

16. A photoconductive composition comprising an organic photoconductor and a cyanine dye sensitizer having a first and a second 5 to 6 membered nitrogencontaining heterocyclic nucleus joined by a methine linkage; the first of said nuclei being selected from the group consisting of a 1-alkoxy-pyridyl nucleus and a 1-alkoxyquinolyl nucleus, each of said first nuclei being joined at the 2-carbon atom thereof to said linkage; and said 65 second nucleus being a heterocyclic nucleus of the type contained in cyanine dyes joined at a carbon atom thereof to said linkage, to complete said cyanine dye.

17. A photoconductive composition in accordance with claim 16 wherein said second nucleus is a thiazole nucleus. $_{70}$

18. A photoconductive composition in accordance with claim 16 wherein said second nucleus is a benzoxazole nucleus.

19. A photoconductive composition in accordance with claim 16 wherein said second nucleus is an indolenine.

wherein:

- Q1 and Q2 each represent the non-metallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus:
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R_2 is selected from the group consisting of an aryl radical, a hydrogen atom and an alkyl radical;
- R₃ is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methine linkage;
- X is an acid anion;
- g is a positive integer from 1 to 2; and
- n is a positive integer from 1 to 4.

24. The electrophotographic element of claim 23 wherein Q₂ represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

25 An electrophotographic element comprsing a support having coated thereon a photoconductive composition comprising an organic photoconductor and a sensitizer having the formula:

$$\begin{array}{c} & \begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ &$$

wherein:

- Q2 and Q3 each represent the non-metallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus:
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R₂, D and E are each selected from the group consist-

75

ing of an aryl radical, a hydrogen atom and an alkyl radical;

- R_3 is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methine linkage;
- X is an acid anion; and
- n is a positive integer from 1 to 4.

26. The electrophotographic element of claim 25 wherein Q_2 represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus.

27. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising an organic photoconductor and a sensitizer 15 having the formula:

$$RO \xrightarrow{\qquad N} I \xrightarrow{\qquad C} C \xrightarrow{\qquad K^{-}} C \xrightarrow{\qquad K^{-$$

wherein:

- Q_2 and Q_7 each represent the non-metallic atoms neces- 25 sary to complete a 5 to 6 membered heterocyclic nucleus;
- R is selected from the group consisting of an alkyl radical and an acyl radical;
- R_2 and J are each selected from the group consisting ³⁰ of an aryl radical, a hydrogen atom and an alkyl radical;
- R_3 is selected from the group consisting of an alkyl radical, an alkenyl radical, an aryl radical and an alkoxy radical;
- L is a methane linkage;
- X is an acid anion;
- m is a positive integer from 1 to 3; and
- g is a positive integer from 1 to 2.

28. The electrophotographic element of claim 27 wherein Q_2 represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus, a quinoline nucleus and an indole nucleus. ber selected from the group consisting of a pyridine

29. An electrophotographic element comprising a support having coated thereon a photoconductive composition comprising an organic photoconductor and a cyanine dye sensitizer having a first and a second 5 to 6 membered nitrogen-containing heterocyclic nucleus joined by a methine linkage; the first of said nuclei being a 1-alkoxy-2-arylindole nucleus joined at the 3-carbon atom thereof to said linkage; and said second nucleus being a desensitizing nucleus joined at a carbon atom thereof to said linkage, to complete said cyanine dye sensitizer.

30. An electrophotographic element in accordance with 55 claim **29** wherein said cyanine dye sensitizer contains a 2-arylindole desensitizing nucleus.

31. An electrophotographic element in accordance with claim **29** wherein said cyanine dye sensitizer contains an imidazo[4,5-b]quinoxaline desensitizing nucleus. 60

32. An electrophotographic element in accordance with claim 29 wherein said cyanine dye sensitizer contains a nitro substituted desensitizing nucleus.

33. An electrophotographic element in accordance with claim 32 wherein said cyanine dye sensitizer contains a 65 6-nitrobenzothiazole desnsitizing nucleus.

34. An electrophotographic element in accordance with claim 22 wherein said desensitzing nucleus is a 5-nitro-2-phenyl indole nucleus.

35. An electrophotographic element comprising a sup- 70 port having coated thereon a photoconductive composition comprising an organic photoconductor and a cyanine dye sensitizer having a first and a second 5 to 6 membered nitrogen-containing heterocyclic nucleus joined by a methane linkage; the first of said nuclei being selected 75

from the group consisting of a 1-alkoxypyridyl nucleus and a 1-alkoxyquinolyl nucleus, each of said first nuclei being joined at the 2-carbon atom thereof to said linkage; and said second nucleus being a heterocyclic nucleus of the type contained in cyanine dyes joined at a carbon

atom thereof to said linkage, to complete said cyanine dye.

36. An electrophotographic element comprising a support in accordance with claim 35 wherein said second nucleus is a thiazole nucleus.

37. An electrophotographic element comprising a support having coated thereon a photoconductive composition in accordance with claim 35 wherein said second nucleus is a benzoxazole nucleus.

38. An electrophotographic element in accordance with claim 35 wherein said second nucleus is an indolenine.

39. An electrophotographic element comprising a support having coated thereon a composition comprising an organic photoconductor and a sensitizer selected from the 20 group consisting of

- (a) 1,1'-dimethoxy-2,2'-diphenyl-3,3'-indolocarbocyanine perchlorate,
- (b) 1-methoxy-1'-methyl-2,2',10-triphenyl-3,3'-indolocarbocyanine perchlorate,
- (c) 3'-ethyl-methoxy-6'-nitro-2-phenyl-3-indolothiacarbocyanine p-toluenesulfonate,
- (d) 1,3-diallyl-1⁻-methoxy-2[']-phenylimidazo[4,5-b] quinoxaline-3[']-indolocarbocyanine perchlorate,
- (e) 1'-methoxy-1,3,3-trimethyl-5-nitro-2'-phenylindo-3'-indolocarbocyanine perchlorate and
- (f) 1-methoxy-1',3',3'-trimethyl-2-phenylindo-2'pyrrolo[2,3-b]pyridocarbocyanine perchlorate.

40. A photoconductive element for use in electrophoto-

grahy comprising a support having coated thereon a 35 photoconductive composition comprising:

- (a) about 10 to 60% by weight based on said photoconductive composition of an organic photoconductor,
- (b) a film-forming polymeric binder for said photoconductor and
- (c) 0.005 to 5% by weight of 1,1'-dimethoxy-2,2'-diphenyl-3,3'-indolocarbocyanine perchlorate.

41. A photoconductive element for use in electrophotography comprising a support having coated thereon a photoconductive composition comprising:

- (a) about 10 to 60% by weight based on said photoconductive composition of an organic photoconductor,
- (b) a film-forming polymer binder for said photoconductor and
- (c) 0.005 to 5% by weight of 1-methoxy-1'-methyl-2,2', 10-triphenyl-3,3'-indolocarbocyanine perchlorate.

42. A photoconductive element for use in electrophotography comprising a support having coated thereon a photoconductive composition comprising:

- (a) about 10 to 60% by weight based on said photoconductive composition of an organic photoconductor,
- (b) a film-forming polmeric binder for said photoconductor and
- (c) 0.005 to 5% by weight of 1,3-diallyl-1'-methoxy-2' - phenylimidazo[4,5-b]quinoxalino - 3' - indolocarbocyanine perchlorate.

43. A photoconductive element for use in electrophotography comprising a support having coated thereon a photoconductive composition comprising:

- (a) about 10 to 60% by weight based on said photoconductive composition of an organic photoconductor.
- (b) a film-forming polymer binder for said photoconductor and
- (c) 0.005 to 5% by weight of 1'-methoxy-1,3,3-trimethyl - 5-nitro-2'-phenylindo-3'-indolocarbocyanine perchlorate.
- 44. A photoconductive element for use in electro-

photography comprising a support having coated thereon a photoconductive composition comprising: (a) about 10 to 60% by weight based on said photo-

- (a) about 10 to 60% by weight based on said photoconductive composition of an organic photoconductor,
- (b) a film-forming polymeric binder for said photo-⁵ conductor and
- (c) 0.005 to 5% by weight of 1-methoxy-1',3',3'-trimethyl - 2-phenylindo-2'-pyrrolo[2,3-b]pyridocarbocyanine perchlorate.

45. An electrophotographic element as described in ¹⁰ claim 20 wherein the organic photoconductor is an organic amine.

46. An electrophotographic element as described in

claim 20 wherein the organic photoconductor is a polyarylalkane.

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CHARLES E. VAN HORN, Primary Examiner

U.S. Cl. X.R.

96-1.5; 260-240, 240.4, 240.6, 240.65

UNITED STATES PATENT OFFICE (5/69) CERTIFICATE OF CORRECTION

Patent No. 3,560,209 Dated February 2, 1971

Inventor(s) Philip W. Jenkins, Donald W. Heseltine and John D. Me

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

Column 15, line 36, claim 27, delete "methane" and insert ---methine---.

Column 15, line 44, claim 28, delete last line of claim 28, "ber selected from the group consisting of a pyridine".

Column 15, line 66, claim 33, delete "desnsitizing" and insert ---desensitizing---.

Column 15, line 75, claim 35, delete "methane" and insert ---methine---.

Signed and sealed this 4th day of May 1971.

(SEAL) Attest:

EDWARD M.FLETCHER, JR. Attesting Officer WILLIAM E. SCHU) Commissioner of