United States Patent [19]
Janssens et al.

[11] **3,830,647**
[45] **Aug. 20, 1974**

[54] RECORDING PROCESS AND ELEMENT EMPLOYING AS PHOTOCONDUCTIVE MATERIAL FLUORENE RING SYSTEM FUSED 1,2,-DIHYDRO-2,2,4-TRIALKYLQUINOLINES

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[73] Assignee: **AGFA-Gevaert N.V.**, Mortsel, Belgium

[22] Filed: **Dec. 10, 1971**

[21] Appl. No.: **206,901**

[30] **Foreign Application Priority Data**

Dec. 11, 1970 Great Britain 59094/70

[52] **U.S. Cl.** .... **96/1.5**, 96/1.6, 96/1.8, 252/501, 260/240 E, 260/240.1, 260/240.5, 260/240.6, 260/240.65

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

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

[56] **References Cited**

UNITED STATES PATENTS

888,016	7/1971	Kalenda	96/126
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FOREIGN PATENTS OR APPLICATIONS

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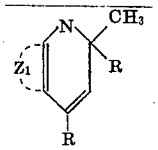
Primary Examiner—Ronald H. Smith
Assistant Examiner—John R. Miller
Attorney, Agent, or Firm—William J. Daniel

[57] ABSTRACT

Photoconductive elements containing a monomeric organic photoconductive compound corresponding to the following general formula:



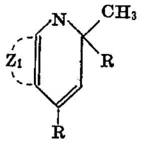
wherein: R represents a $(C_1$-$C_4)$ alkyl radical, and Z_1 represents the necessary atoms to close an adjacent ring system of the fluorene series, are described. The described photoconductors can be chemically and spectrally sensitized and charged either negatively or positively.

33 Claims, No Drawings

RECORDING PROCESS AND ELEMENT EMPLOYING AS PHOTOCONDUCTIVE MATERIAL FLUORENE RING SYSTEM FUSED 1,2-DIHYDRO-2,2,4-TRIALKYL-QUINOLINES

This invention relates to recording and reproduction of information-wise modulated electromagnetic radiation and to recording materials suitable therefor, and particularly relates to such processes and recording materials containing one or more organic photoconductive compounds as hereinafter described.

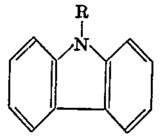
It has now been found that an efficient photoconductive particularly photosensitive recording member can be formed by using in its composition a photoconductive compound corresponding to the following general formula:



wherein:

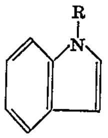
R represents a C_1-C_4 alkyl radical, for example methyl, ethyl, propyl or butyl, preferably a methyl radical, and

Z_1 represents the necessary atoms to close an adjacent polynucleic ring system of the indene or fluorene series or an adjacent polynucleic heterocyclic ring system including these ring systems substituted with substituents having a nonionic character. For example Z_1 represents the necessary atoms to close an adjacent heterocyclic ring system of one of the following classes represented by structural formulae including the substituted derivatives having substituents with non-ionic character:



wherein:

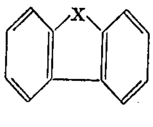
R represents hydrogen or an alkyl group, e.g., a methyl or ethyl group.



(indole)

wherein:

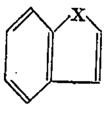
R represents hydrogen or an alkyl group, e.g., a methyl or an ethyl group.



(dibenzofuran)
(dibenzothiophene)

wherein:

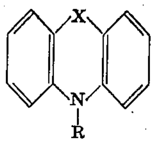
X represents oxygen or sulphur



(benzofuran)
(benzothiophene)

wherein:

X represents oxygen or sulphur

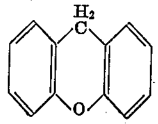


(phenothiazine)
(phenoxazine)

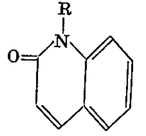
wherein:

X represents oxygen or sulphur, and

R represents hydrogen or an alkyl group, e.g., a methyl group or ethyl group.



(xanthene)



(quinoline-2-one)

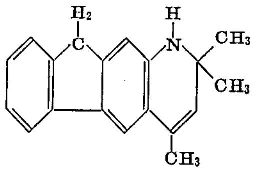
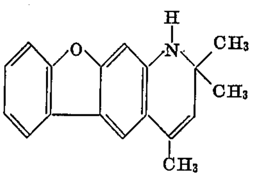
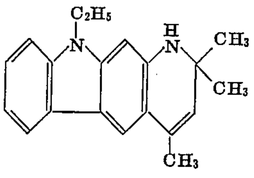
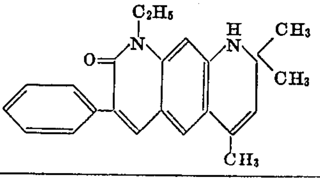
wherein:

R represents hydrogen or an alkyl group, e.g., a methyl or ethyl group

Examples of such non-ionic substituents are: an alkyl group, e.g., methyl, halogen, e.g., fluorine, chlorine, bromine or iodine, a nitro group, an alkoxy group, e.g., methoxy, an amino group, a substituted amino group, e.g., a monoalkylamino or dialkylamino group or a cyano group.

Specific examples of the present photoconductive compounds of which the compounds containing the atoms represented by Z_1 to close an adjacent heterocyclic nucleus are considered as new compounds are listed in the following table.

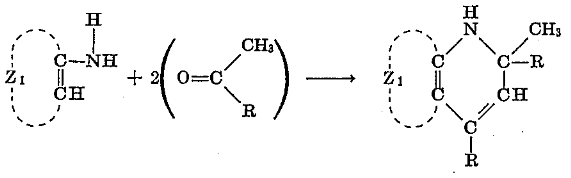
TABLE I

Number	Formula
1	
2	
3	
4	

The preparation of the 1,2-dihydro-2,2,4-trialkylquinolines used according to the present invention proceeds advantageously by condensing a primary amino compound in which the primary amino group is present on an aromatic nucleus with an aliphatic ketone containing at least one methyl group linked directly to the carbonyl group of the ketone in a preferred molar ratio of at least 1:2 in the presence of a suitable catalyst, such as toluene sulfonic acid, benzene sulfonic acid, sulfuric acid, iodine or bromine.

Examples of suitable ketones are acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl butyl ketone.

The production of the organic photoconductors is illustrated by the following reaction scheme:



in which Z_1 and R have the same meaning as described above.

The following preparations illustrate in more details the manufacture of the compounds enumerated in the Table.

Preparation of Compound 1

In a mixture of 30 g of 2-amino-fluorene and 0.6 g of iodine heated at 170°C was passed dropwise acetone for a period of 6 h. The obtained product was dried under reduced pressure to remove any acetone left.

Yield: 98 percent.

Melting point: 171°C.

Preparation of Compound 2

A mixture of 0.25 mole of 2-amino-diphenylene oxide, 1 g of iodine and 2 mole of mesityloxide was heated for 12 h on an oil-bath of 140°C. The acetone produced in the reaction was separated through a dephlegmator.

The obtained reaction mixture was subjected to diminished pressure to remove the volatile products. The residue was dissolved in methylene chloride and washed in subsequent order

- 3 times with 5N aqueous hydrochloric acid
- 3 times with an aqueous 30 percent sodium hydroxide solution
- 3 times with water.

The methylene chloride solution was dried on anhydrous sodium sulphate and the solvent driven off.

The residue was purified by column chromatography using a column provided with silica gel as adsorbers and as eluent a mixture of methylene chloride/benzene (8:2 by volume). This purification was repeated twice.

Yield: 5 g. Oily product.

Preparation of Compound 3

A mixture of 0.1 mole of 1-ethyl-4-amino carbazole, 0.65 g of iodine and 100 ml of diacetone alcohol was refluxed on an oil bath for 3 days and meanwhile diacetone alcohol added dropwise below the surface of the liquid mass. Simultaneously the produced acetone was separated by means of a dephlegmator.

The obtained reaction mixture was subjected to diminshed pressure to further remove the volatile products. The residue was dissolved in methylene chloride and washed in subsequent order:

- 3 times with 5N aqueous hydrochloric acid.
- 3 times with an aqueous 30 percent sodium hydroxide solution
- 3 times with water.

The methylene chloride solution was dried on anhydrous sodium sulphate and the solvent driven off.

The residue was purified by boiling it three times with a small amount of a petroleum fraction boiling between 80°–120°C and active carbon.

Yield: 4 g. Melting point: < 50°C.

Preparation of Compound 4

A mixture of 0.1 mole of 1-ethyl-3-phenyl-7-amino-quinoline 2-one, 0.65 g of iodine and 100 ml (0.8 mole) of diacetone alcohol was heated for 72 h on an oil bath. The acetone produced in the reaction was separated through a dephlegmator. After the second day still 100 ml of diacetone alcohol was added through the inlet pipe of a dropping funnel ending below the surface of the reaction liquid.

The reaction product was purified as described for compound 3. Yield: 5 g. Oily product.

The photoconductive compounds applied according to the present invention may be used alone or in combination with substances imparting desired chemical or physical properties to the recording element. So, these substances can be combined with other substances that either or not are photoconductive and exert an influence, e.g., on the dark-resistivity, the dischargeability or conductivity of the recording layer by an exposure to electromagnetic radiation, or on the transparency or the quality of the final image, e.g., by counteracting the fringe effect as described in the United Kingdom Pat. specification 1,007,349 filed Oct. 12, 1961 by Gevaert Photo-Producten N.V.

A proper combination with selected binding agents and/or chemical sensitizing agents may result in an enhancement of the total sensitivity. The recording elements according to the present invention preferably contain at least 5 percent by weight of a photoconductive 1,2-dihydroquinoline derivative being within the scope of the above general formulae. For use in electrophotography the recording element preferably consists for at least 10 percent by weight of one or more of the said 1,2-dihydroquinoline derivatives. The electrically insulating binding agent used in a recording layer containing said derivative may provide the desired mechanical strength for instance to form a self-supporting layer, and preferably has a resistivity of at least 10^9 ohm.cm.

According to a particular embodiment the recording layer consists of the photoconductor, which, e.g., has been applied to a suitable support in molten state forming a micro-crystalline or glass-like layer on cooling. This technique can be applied when the photoconductive recording element has not to possess a high mechanical strength. For such technique reference is made to the Canadian Pat. specification 712,541 filed Feb. 5, 1960 by Gevaert Photo-Producten N.V.

Macromolecular compounds suitable for use as insulating binding agent for the photo-conductive compounds are, e.g., natural resins such as dammar resin, gum arabic, microcrystalline waxes, modified natural substances such as cellulose diacetate, cellulose triacetate, and ethyl cellulose, pentaerythrite polyesters or modified colophony resins and ester gums, polymers such as polyethylene, polystyrene and copolymers of styrene, polyvinyl acetate and copolymers of vinyl acetate, polyvinyl acetals of formaldehyde, acetaldehyde or butyraldehyde, polyacrylic acid esters and polymethacrylic acid esters, coumarine-indene resins epoxy resins and polycondensates such as glycerol-phthalate resins and other glyceryl polyesters, alkyd resins, diethylene glycol polyesters, formaldehyde resins and silicone resins.

Preferred binding agents are halogen-containing polymers and epoxy resins combined with silicone resins. The sensitization of organic photoconductors with halogen-containing polymers is described in the United Kingdom Pat. specification 964,878 filed May 3, 1960 by Gevaert Photo-Producten N.V. According to said specification a material suitable for use in electrophotography comprises a photoconductive layer incorporating an organic monomeric photoconductor and a halogen-containing polymer in such layer or in a juxtaposed layer (if any), the sensitivity of said photoconductor having been increased by making it to interact with said halogen-containing polymer by heating.

In the following Table II a list of preferred polymeric binding agents is given, which may be used in combination with the heterocyclic organic photoconductors of use according to the present invention as well as the corresponding suitable solvents.

TABLE II

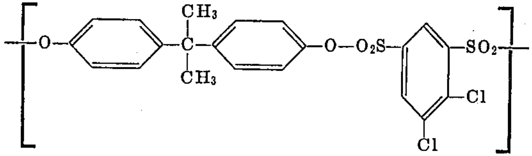
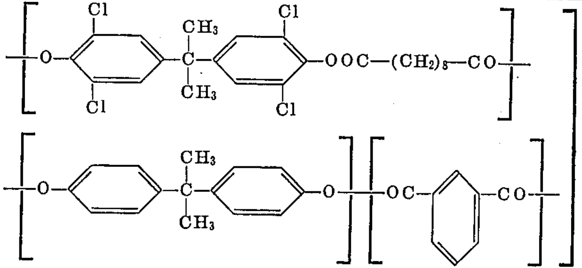
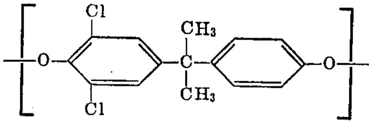
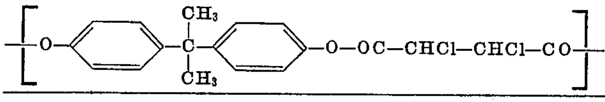
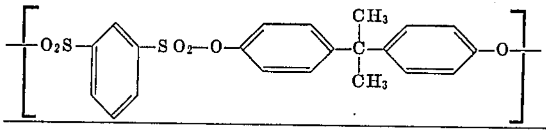
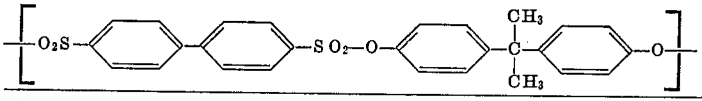
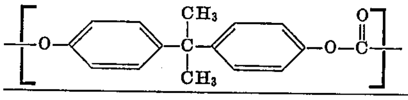
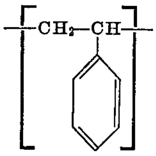
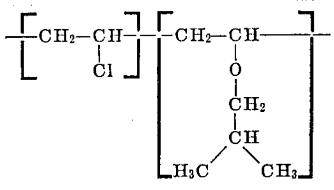
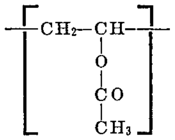
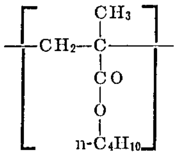
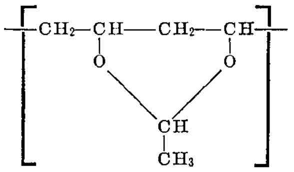
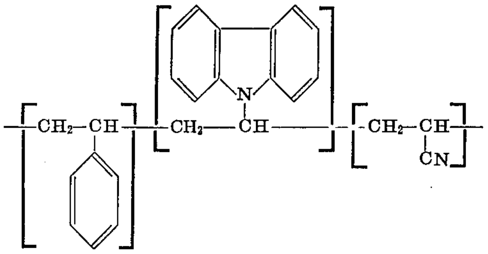
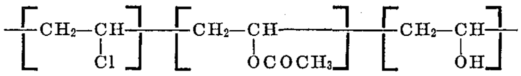
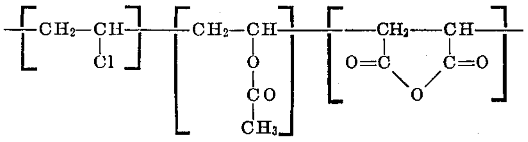
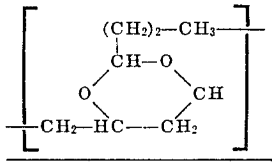
Polymeric binding agent defined by its structural unit(s)	Solvent
	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
$-\left[O-(CH_2)_6-OOC-(CH_2)_8-CO\right]-$	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
	Methylene chloride.

TABLE II – Continued

Polymeric binding agent defined by its structural unit(s)	Solvent
 25% by weight	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
	Methylene chloride.
 10% by weight 80% by weight 10% by weight	Methylene chloride.
 91% by weight 3% by weight 6% by weight	Methylene chloride/acetone (1:1).
 85% by weight 14% by weight 1% by weight	Methylene chloride/acetone (1:1).
	Methylene chloride/acetone/ethanol (1:1:1).

The photoconductive compounds applied according to the present invention can be used in admixture with other known inorganic and organic photoconductive substances, e.g., sulphur, selenium, photoconductive oxides, sulphides, and selenides of zinc, cadmium, mercury, antimony, bismuth, lead, anthracene, anthraquinone, and photoconductive polymers, e.g., those containing N-vinylcarbazole recurring units and other known monomeric and polymeric organic photoconductors, e.g., those described in the published Dutch

Pat. application 70/04174 filed Mar. 24, 1970 by Gevaert-Agfa N.V.

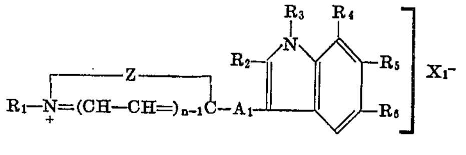
The inherent spectral sensitivity of most of the photoconductive compounds listed in Tables I and II is mainly situated in the near U.V. range, i.e., in the range of 360 to 420 nm.

The spectral sensitivity of recording materials according to the present invention can be increased in different ways, e.g., by adding so-called spectral sensitizing agents for the photoconductive substances contained in the recording element or by admixing to the said heterocyclic organic photoconductive compounds other photoconductive substances, the inherent sensitivity of which for a particular part of the electromagnetic radiation spectrum is higher than that of the present compounds.

So, according to a special embodiment of the present invention semi-transparent recording layers are prepared, in which said heterocyclic photoconductive compounds are used in admixture with (an) inorganic photoconductive substance(s), especially photoconductive substances of the group of zinc oxide, photoconductive lead(II) oxide and photoconductive cadmium sulphide or cadmium selenide.

Suitable spectral sensitizing dyestuffs for the organic photoconductor are among others organic dyestuffs, known as methine dyes, or xanthene dyes of which the phthaleins and rhodamines are subclasses, and triarylmethane dyes, e.g., crystal violet (C.I. 42,555) and the triarylmethane dyes described in published Dutch Pat. application 6704706 filed Apr. 3, 1967 by Gevaert-Agfa N.V. The term methine dyes includes mono- as well as polymethine dyes which dyes are known to those skilled in the art of the spectral sensitization of light-sensitive silver halide. Preferred methine dyes are of the cationic type. As preferred xanthene dyes Rhodamine B (C.I. 45,170), Rose Bengale (C.I. 45,440) and Fluorescein (C.I. 45,350) are mentioned. The spectral sensitizing dyes are preferably added to the recording layer composition in a proportion of 0.01 to 5 percent by weight in respect of the photoconductive substance(s).

Particularly preferred methine dyes are within the scope of the following general formulae:



wherein:

A_1 stands for a dimethine or tetramethine group including a substituted dimethine or tetramethine group,

n stands for 1 or 2,

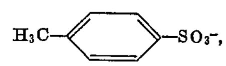
R_1 stands for alkyl including substituted alkyl, an unsaturated aliphatic group, e.g., allyl, aralkyl including substituted aralkyl, aryl including substituted aryl or cycloalkyl,

R_2 stands for alkyl, aryl including substituted aryl, e.g., phenyl and phenyl substituted preferably in the p-position by alkyl, halogen and alkoxy, a 5- or 6-membered heterocycle the heteroatom of which is oxygen, sulphur, selenium or nitrogen such as 2-, 3-, or 4-pyridyl, 2-furyl, 2-thienyl, etc. including their quaternary salts,

R_3 stands for hydrogen or has one of the meanings given for R_1,

R_4 stands for hydrogen, alkyl, alkoxy or halogen or together with R_3 forms an alkylene bridge such as dimethylene and trimethylene,

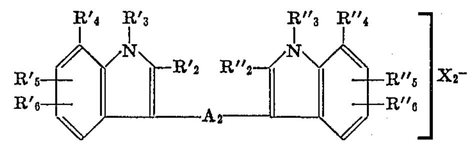
each of R_5 and R_6 (the same or different) stands for hydrogen, alkyl, alkoxy or halogen or together represent the atoms necessary to complete a fused-on benzene nucleus; X_1^- represents an anion, e.g., Cl^-, Br^-, I^-, ClO_4^-, $CH_3SO_4^-$, or



but is missing when the R_1 group contains already an anion (betaine type salt), and Z represents the atoms necessary to complete a heterocyclic nucleus of the types used in the production of cyanine dyes e.g. such as those of the thiazole series, e.g., thiazole, 4-methylthiazole, 4-methyl-5-carbethoxythiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4-(p-tolyl)-thiazole, 4-(p-bromophenyl)-thiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)-thiazole, 4-(m-nitrophenyl)-thiazole, those of the benzothiazole series, e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 6-sulphobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, 4,5,6,7-tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, 5,6-dimethylbenzothiazole, those of the naphthothiazole series, e.g., naphtho[2,1-d]thiazole, naphtho [1,2-d]thiazole, 5-methoxynaphtho[1,2-d]-thiazole, 5-ethoxynaphtho[1,2-d]-thiazole, 3-methoxynaphtho[2,1-d]-thiazole, 7-methoxynaphtho[2,1-d]-thiazole, those of the thionaphtheno [7,6-d]-thiazole series, e.g., 7-methoxythionaphtheno[7,6-d]-thiazole, those of the thiadiazole series, e.g., 4-phenylthiadiazole, those of the oxazole series, e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, those of the benzoxazole series, e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, those of the naphthoxazole series, e.g., naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, those of the selenazole series, e.g., 4-methylselenazole, 4-phenylselenazole, those of the benzoselenazole series, e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-methyl-6-methoxybenzoselenazole, 5,6-dioxymethylenebenzoselenazole, 5-hydroxybenzoselenazole, 4,5,6,7-tetrahydrobenzoselenazole, those of the naphthoselenazole series, e.g., naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, those of the thiazoline series, e.g., thiazoline, 4-methylthiazoline, 4-hydroxymethyl-

4-methylthiazoline, 4,6-bis-hydroxymethylthiazoline, those of the oxazoline series, e.g., oxazoline, those of the selenazoline series, e.g., selenazoline, those of the 2-quinoline series, e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc., those of the 4-quinoline series, e.g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, those of the 1-isoquinoline series e.g. 1-isoquinoline, 3,4-dihydroisoquinoline, those of the 3-isoquinoline series, e.g., 3-isoquinoline, those of the pyrimidine series, those of the quinoxaline series, those of the quinazoline series, those of the 1-phthalazine series, those of the 2-pyridine series, e.g., pyridine, 5-methylpyridine, 3-nitropyridine, those of the 3,3-dialkylindolenine series, e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc., those of the benzimidazole series, e.g., benzimidazole, 5,6-dichlorobenzimidazole, 5-chlorobenzimidazole, 5,6-dibromobenzimidazole, 5-chloro-6-aminobenzimidazole, 5-chloro-6-bromobenzimidazole, 5-phenylbenzimidazole, 5-fluorobenzimidazole, 5,6-difluorobenzimidazole, 5-cyanobenzimidazole, 5,6-dicyanobenzimidazole, 5-chloro-6-cyanobenzimidazole, 5-fluoro-6-cyanobenzimidazole, 5-acetylbenzimidazole, 5-chloro-6-fluorobenzimidazole, 5-carboxybenzimidazole, 7-carboxybenzimidazole, 5-carbethoxybenzimidazole, 7-carbethoxybenzimidazole, 5-sulphamylbenzimidazole, or 5-N-ethylsulphamylbenzimidazole, 5-ethylsulphonylbenzimidazole and 5-trifluoromethylsulphonylbenzimidazole;

II.



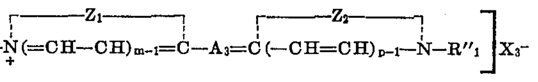
wherein:

A_2 stands for a monomethine or trimethine group including a substituted monomethine or trimethine group,

each of R'_2 - R'_6 and R''_2 - R''_6 (the same or different) has one of the meanings given for R_2 - R_6,

X_2^- has the same significance as X_1^-;

III.



$$\left[R'_1-\overset{+}{N}(=CH-CH)_{m-1}=C-A_3=C(-CH=CH)_{p-1}-N-R''_1\right]X_3^-$$

wherein:

each of R'_1 and R''_1 (the same or different) has one of the meanings given for R_1,

X_3^- has the same meaning as X_1^-,

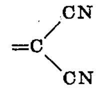
A_3 has the same meaning as A_2;

each of m and p (the same or different) stands for 1 or 2, and

each of Z_1 and Z_2 (the same or different) stands for the atoms necessary to complete a heterocyclic nucleus of the thiazole, benzothiazole, naphthothiazole, thionaphtheno[7,6-d]-thiazole, thiadiazole, oxazole, benzoxazole, naphthoxazole, selenazole, benzoselenazole, naphthoselenazole, 2-quinoline, 4-quinoline, pyrimidine, quinoxaline, quinazoline, 2-pyridine, 3,3-dialkylindolenine or of the benzimidazole series; representative examples of these heterocyclic nuclei can be found above in the definition of Z in formula I.

The dyestuffs corresponding to the above general formulae can be prepared according to the methods known by those skilled in the art of methine dye chemistry.

According to a further embodiment of the invention, the recording material contains one or more substances that increase the photoconductivity of the recording material in the inherent spectral sensitivity range of the said heterocyclic organic photoconductive compounds. As already has been said a binding agent can act as a sensitizing agent that enhances the total sensitivity of the recording element. In addition are to be mentioned compounds containing one or more electron-attracting atoms or groups, e.g., those that are known as non-ionic Lewis acids, e.g., the Lewis acids that can form a "charge transfer complex" as described in U.S. Pat. specification 3,408,183 of Joseph Mammino issued Oct. 29, 1968. Good sensitizing results are obtained with organic carboxylic acid anhydride compounds and with quinones containing electron-attracting substituents, e.g. halogen or cyano, such as in tetrachlorobenzoquinone, tetracyanobenzoquinone and in organic compounds containing a



group, and with the compounds according to the structural formula of the Belgian Pat. specification 734,141 filed June 6, 1969 by Gevaert-Agfa N.V. and the chlorine- and/or cyano-containing plymers of Table II.

The 1,2-dihydroquinoline derivatives may be used in admixture with diazonium salts that on exposure to electromagnetic radiation produce (a) radical(s) that irreversibly increase(s) the electro-conductivity of a recording layer. Such substances as well as details about their incorporation into a recording layer containing an organic photoconductive insulating substance are described in the United Kingdom Pat. specification 964,872 filed Apr. 22, 1959 by Gevaert Photo-Producten N.V. and the U.S. Pat. specification 3,113,022 of Paul Maria Cassiers, Jean Marie Nys, Jozef Frans Willems and Rene Maurice Hart issued Dec. 3, 1963. A particularly suitable conductivity-increasing diazonium compound is p-nitrobenzene-diazonium chloride. The diazonium compounds are preferably used in an amount of 0.01 percent to 10 percent by weight in respect of the present photoconductive heterocyclic organic compounds.

Other additives well known in the art of preparing photoconductive coatings for recording purposes may be used, e.g., matting agents, fluorescing compounds, phosphors, optical brightening agents, agents controlling the adhesive power of the recording layer, agents controlling the elasticity, the plasticity and the hardness of the recording layer, agents controlling the viscosity of the coating composition, antioxidants, gloss-improving agents, etc.

Transparent and semi-transparent recording materials containing the photoconductive heterocyclic organic compounds as described hereinbefore are especially suited for use in recording materials applied for the production and reproduction of microfilm images.

Microfilm images can be copied in contact or enlarged optically on recording materials according to the present invention. According to the type of development, the transparencies obtained (contact copies and enlargements) can serve as negative or positive intermediate prints for further printing, e.g., on diazotype materials.

The semitransparent recording materials according to the present invention preferably have an optical density not larger than 0.30 towards visible light or the copying light used in the printing apparatus wherein it is used as intermediate print.

The photoconductive heterocyclic organic compounds described hereinbefore are further especially suited for being applied in the manufacture of pigment images wherein the latter may have the properties of a fluorescent compound or phosphor. As is generally known luminexcent phosphors are used in screens of cathode-ray tubes and more particularly in television, X-ray, radar and oscilloscope screens.

In colour television screens phosphors of different colour have to be fixed on a screen in a particular pattern.

The described photoconductive compounds are successfully used in a process for the production of colour television screens as described in the French Pat. Specification 1,336,499 filed Sept. 26, 1962 by Comp. Francaise Thomson-Houston. According to the process described in said specification a pattern of a phosphor on a screen support is produced by the steps of applying to said support a coating of an electroconductive material and to said coating a layer comprising a vaporisable or thermolysable photoconductive compound optionally incorporated in a vaporisable or thermolysable binding agent. On said coating an electrostatic charge pattern corresponding with the pigment pattern to be produced is formed in an electrophotographic way, and the electrostatic charge pattern is developed with nonvolatile powder particles that have the desired phosphorescent or luminescent properties. Subsequently the photoconductive layer containing the phosphor powder image is heated in order to remove the volatile substances of the photoconductive recording layer and to make the phosphor pattern adhere to the screen support.

In order to fix the powder image before applying the heating step it is preferably overcoated with a layer of a thermolysable binding agent.

According to said French Patent Specification photoconductors of the group of anthracene, anthraquinone and xanthene are used. The recording layer may further contain boric acid.

The photoconductors mentioned in the French Patent Specification are advantageously partly or wholly substituted by the photoconductive substances applied according to the present invention.

Suitable thermolysable binding agents belong to the class of the polyacrylic acid esters and polymethacrylic acid esters, e.g. polymethyl methacrylate, polyethyl methacrylate and polyethyl acrylate.

The thickness of the photoconductive layers of the present invention is not critical but is open to choice within a wide range according to requirements in each individual case. Good results are attained with photoconductive layers of a thickness between 1 and 30 μ preferably between 2 and 20 μ. Too thin layers do not have a sufficient insulating power in the absence of active electromagnetic radiation, whereas too thick layers require extensive exposure times.

In the manufacture of electrophotographic recording materials according to the present invention a relatively conductive support for the recording layer is used, e.g., an electroconductive sheet or plate, or an insulating sheet or plate covered with an electroconductive interlayer. By electro-conductive plate or sheet is understood a plate or sheet those electrical resistivity is smaller than that of the non-irradiated (dark-adapted) photoconductive layer, i.e., in general smaller than 10^9 ohm.cm and preferably is at least 100 times as small as that of the recording layer. Supports whose resistivity is not higher than 10^7 ohm.cm are preferred. The recording layers themselves have preferably an electrical insulating power as high as possible without affecting too much the photosensitivity by means of too high an amount of insulating binding agent. Preferably the recording layers have in non-irradiated state (dark-adapted state) a resistivity of at least 10^9 ohm.cm.

Suitable conductive plates are, e.g., plates of metals such as aluminium, zinc, copper, tin, iron, or lead.

Suitable electro-conductive interlayers for insulating supports are, e.g., vacuum-coated metal and conductive metal compound (metal oxide or metal salt) layers such as silver, tin, aluminium, titanium dioxide and copper iodide conductive layers, transparent conductive polymer layers, e.g., applied from polymers containing quaternized nitrogen atoms, such as those described in the United Kingdom Pat. Specification 950,960 filed Sept. 23, 1960 by Gevaert Photo-Producten N.V., or layers containing conductive particles, e.g. carbon black and metal particles dispersed in a binder. The binder used for said particles has a resistivity preferably lower than 10^6 ohm.cm. A suitable binder for that purpose is gelatin.

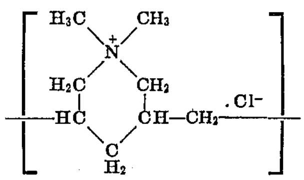
It is possible to produce transparent photoconductive recording materials by applying the photoconductive compounds together with a suitable binder (if necessary) from a clear solution to a conductive transparent base or a transparent insulating base coated with an electroconductive transparent interlayer.

As transparent bases resin sheets having an optical density of not more than 0.10 are preferred, e.g., a sheet made of polyethylene terephthalate or cellulose triacetate. The conductive interlayer preferably consists of a metal coating, e.g., a vacuum-coated aluminium layer having an optical density of not more than 0.30, or of a conductive transparent polymer layer composed, e.g., of an organic polyionic polymer, e.g., a polymer containing quaternized nitrogen atoms such as a quaternized polyethylene-imine.

In reproduction techniques wherein the prints are to be produced on an opaque background preferably a paper sheet is used as support for the recording layer.

Paper sheets that have an insufficient electrical conductivity are coated or impregnated with substances enhancing their conductivity, e.g., by means of a conductive overcoat such as a metal sheet laminated thereto.

As substances suited for enhancing the conductivity of a paper sheet and which can be applied in the paper mass are particularly mentioned hygroscopic compounds and antistatic agents as described, e.g., in the United Kingdom Patent Specification 964,877 filed May 2, 1960 by Gevaert Photo-Producten N.V., and antistatic agents of polyionic type, e.g., CALGON CONDUCTIVE POLYMER 261 (trade mark of Calgon Corporation, Inc. Pittsburgh, Pa., U.S.A.) for a solution containing 39.1 percent by weight of active conductive solids, which contain a conductive polymer having recurring units of the following type:



Paper sheets are preferably impermeabilized to organic solvents, e.g., by means of a water-soluble colloid or by strongly hydrating the cellulose fibers such as in the case of glassine paper.

In order to prepare an electrophotographic material according to the present invention various techniques may be applied.

In practice, the photoconductive substances involved, either alone or together with other additives such as those described above, preferably are first dissolved or dispersed in a suitable organic solvent such as a chlorinated hydrocarbon, e.g., methylene chloride. The solution or dispersion thus obtained is uniformly spread on a surface of a suitable support, e.g., by centrifuging, spraying, brushing, or coating. Thereupon the layer formed is dried in such a way that a solid photoconductive layer is formed on the surface of the support.

Recording materials according to the present invention can be used in any of the different techniques known in recording with the aid of photoconductors. According to a preferred embodiment they are used in a technique based on the discharge of an electrostatically charged recording layer by exposure to light.

Photoconductive recording materials prepared according to the present invention can be used in exposure units equipped with incandescent lamps, so that they need not be exposed with light rays rich in ultraviolet such as those emitted by a high-pressure mercury vapour bulb.

The electrostatic charging of photoconductive recording elements according to the present invention can be effected according to any method known in electrophotography, e.g., by friction with a smooth material, with a material possessing a high electric resistance, e.g., a cylinder coated with polystyrene, by corona discharge, by contact charge, or by discharge of a capacitor.

Recording materials according the said organic photoconductive substances can be used in a recording technique comprising a negative corona charging as well as in a recording technique comprising a positive corona charging.

In order to obtain an electrostatic image it is possible to effect the charging and exposure steps simultaneously and even to expose the recording layer imagewise before charging since a conductivity image is formed that is not destroyed immediately, especially if diazonium salts are used in the recording element. It is preferred, however, that the charging is effected before image-wise exposure.

The electrostatic latent image can be converted into a visible image either on the electrophotographic material wherein the latent image was formed, or on a material to which the electrostatic latent image was transferred, e.g., by application of the method described in the Belgian Pat. Specification 529,234 filed May 29, 1954 by Chester Floyd Carlson.

The conversion of the original or transferred latent image into a visible image can occur according to one of the techniques known in electrophotography, wherein use is made of a conductivity pattern (e.g., electrolysis) or the electrostatic attraction or repulsion of finely divided coloured substances, which, e.g., are present in a powder mixture, in an electrically insulating liquid (e.g., in the form of a suspension) or in a gas (e.g., in the form of an aerosol), or wherein electrostatic attraction is used for selectively wetting charged portions of the recording layer, as described in the United Kingdom Pat. Specifications 1,020,505 filed Nov. 8, 1961 and 1,033,419 filed Nov. 26, 1962 both by Gevaert Photo-Producten N.V.

When the sign of the charge of the developing powder or developing liquid is properly chosen, either a negative or a positive print can be obtained from any original. If both printing material and developing powder or developing liquid have the same sign of charge, the powder only adheres to the discharged areas so that a negative print is obtained. If the signs of the recording material and of the developing powder or developing liquid differ, a positive print is obtained.

If a coloured powder is used for making visible the latent image, the visible image obtained can, if necessary, be fixed according to one of the methods known in electrophotography, e.g., by heating, or it can be transferred to another support, e.g., according to the method described in the United Kingdom Pat. Specification 658,699 filed Apr. 14, 1949 by Battelle Memorial Institute and fixed thereon.

The present heterocyclic organic photoconductive compounds can also be supplied in a thermoplastic recording process to form a ripple-image as described, e.g., in the United Kingdom Pat. Specification 964,881 filed May 17, 1960 by Gevaert Photo-Producten N.V.

Evidently the present invention by no means is limited to one or other particular embodiment of using the electrophotographic material containing the photoconductive compounds as described herein. The exposure technique, the charging method, the formation of the charge pattern, the transfer of such pattern if applied, the developing method, and the fixation or the transfer of the developing material pattern may be modified or adapted.

The composition of the recording materials used in these methods may be adapted to the requirements of the recording process used.

Electrophotographic materials according to the present invention can be employed in reproduction techniques, wherein different kinds of electromagnetic radiations are used, e.g., visible light, U.V.-radiation, X-rays and γ-rays.

The following examples illustrate the present invention.

Example 1

To a polyethylene terephthalate support of 100 μ a conductive transparent coating was applied from an aqueous solution of gelatin and CALGON CONDUCTIVE POLYMER 261 (trade name) in a weight ratio of 2:1. The coating was carried out in such a way that the dried coating contained 2 g of gelatin per sq.m. The electrical resistivity of the coating was 5×10^6 ohm per sq.cm.

An electrophotographic recording material was prepared by coating onto said conductive layer a solution containing:

one of the photoconductive compounds listed in the Table I	5 g
copoly(vinyl chloride/vinyl acetate/maleic anhydride)(mol ratio: 86.5/13.3/0.2)	5 g
methylene chloride	100 ml

The solution was applied in such a ratio that the dried recording layer contained 3 g per sq.m of said photoconductive compound.

After a negative corona charging with a potential difference of −6,000 V between the corona wires and the ground, the charged recording layer was contact-exposed for 30 sec. through a step wedge of increment 0.2 with incandescent bulbs that together represent 100 Watt and were placed at a distance of 30 cm.

After exposure the development was carried out with an electrophoretic developer containing positive toner particles and which was prepared by diluting the concentrated developer composition described hereinafter in a volume ratio of 15/1,000 by means of ISOPAR H (trade name for an isoparaffinic hydrocarbon mixture having a boiling range of 177°–188°C sold by Esso Belgium, N.V., Antwerp, Belgium):

carbon black (average particle size: 20 nm)	30 g
zinc monotridecyl phosphate as dispersing agent	1.5 g
ISOPAR H (trade name)	750 ml
resin solution prepared as described hereinafter	150 g

The resin binder solution was prepared by heating 500 g of ALKYDAL L 67 (trade name of Farbenfabriken Bayer A.G., Leverkusen, W. Germany, for a linseed oil-modified (67 percent by weight alkyd resin)) and 500 ccs of white spirit containing 11 percent by weight of aromatic compounds at 60°C till a clear solution was obtained, and subsequent cooling.

The development was carried out by means of developing electrode placed at a distance of 3 mm from the material.

The speed of the developed samples is expressed by the number of the steps that is not covered with developer material.

The following Table III lists the relative speed values for these coatings.

Table III

No. of the photoconductive compound of the Table	No. of non-developed steps
1	8
2	4
3	8
4	1

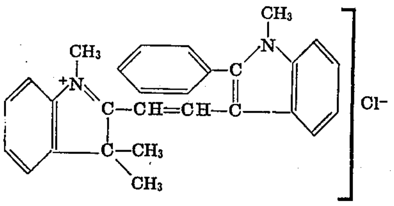
Example 2

The following composition was coated on an aluminium laminated paper:

compound 1 of the Table	6 g
copoly(vinyl chloride/vinyl acetate/maleic anhydride) (mol ratio: 86.5/13.3/0.2)	4 g

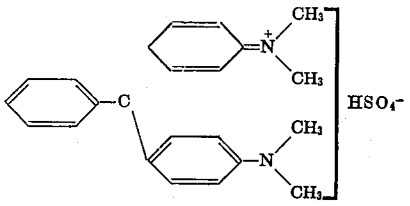
As spectral sensitizing agents:

Orange Astrazon R (C.I. Basic Orange 22; C.I. 48,040) having the folllowing structural formula:



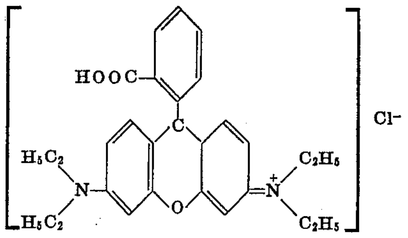
0.10 g.

Brillant Green YS (C.I. Basic Green 1; C.I. 42,040) having the following structural formula:



0.032 g

Rhodamin B (C.I. Basic Violet; C.I. 45,170) having the following structural formula:



0.020 g

sym.-dichloroethane	90 ml
methylene chloride	10 ml

The coating was carried out in the way described in Example 1.

The dried coating was negatively corona charged with a potential difference of −6,000 V between the corona wires and the ground. The charged recording layer was contact-exposed for 5 sec. through a stepwedge having an increment 0.2 using tungsten filaments lamps that together represent 100 Watt and were placed at a distance of 30 cm.

The electrophoretic development was carried out as described in Example 1. Compared with a same non-spectrally sensitized coating the total sensitivity of the spectrally sensitized coating was 60 times higher.

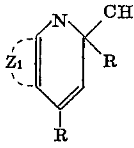
Example 3

To the coating composition of Example 2, 0.25 g of 2,3-dicyano-p-quinone as chemical sensitizer and compound with strongly electronegative groups was added.

The corona charging, image-wise exposure and development were the same as in Example 2. The speed of the recording layer was found to be 2.5 times higher than that of Example 2.

We claim:

1. In a recording process wherein a photoconductive insulating recording layer is exposed to an electromagnetic radiation image to produce an imagewise pattern of increased conductivity in said photoconductive recording element and said conductivity pattern is developed to produce a record of said image, the improvement wherein said element comprises an organic photoconductive compound corresponding to the following general formula:



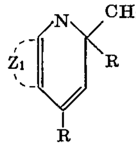
wherein:

R represents a $(C_1$-$C_4)$ alkyl radical, and

Z_1 represents the necessary atoms to close an adjacent ring system of the fluorene series, and a spectral sensitizing agent.

2. A recording process according to claim **1**, wherein R represents a methyl group.

3. A method for recording and reproducing information comprising the steps of producing an electrostatic charge pattern by electrostatically charging and information-wise exposing to electromagnetic radiation a recording element containing a photoconductive compound corresponding to the following general formula:



wherein:

R represents a $(C_1$-$C_4)$ alkyl radical, and

Z_1 represents the necessary atoms to close an adjacent ring system of the fluorene series and a spectral sensitizing agent producing thereby an information-wise increase of the conductivity in the recording element, and developing the resulting latent electrostatic charge pattern with a substance that can be electrostatically attracted.

4. A process according to claim **1**, wherein the recording element is a recording layer that has been applied to a conductive layer or support having a resistivity lower than that of the dark adapted recording element.

5. A process according to claim **4**, wherein the conductive layer or support has a resistivity at least 10^2 lower than that of the recording element in the dark.

6. A process according to claim **4**, wherein the support is a paper support.

7. A process according to claim **4**, wherein the support is an insulating transparent resin support coated with a transparent electroconductive interlayer.

8. A process according to claim **1**, wherein the photoconductive compound is used in admixture with a polymeric binding agent.

9. A process according to claim **8**, wherein the photoconductive compound is used in admixture with a halogen-containing polymer, an epoxy resin and/or silicon resin.

10. A process according to claim **1**, wherein the photoconductive compound is used in admixture with an organic binding agent increasing the photosensitivity of the recording element.

11. A process according to claim **10**, wherein said spectral sensitizing agent is an organic dye.

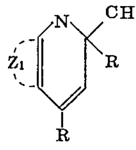
12. A process according to claim **1**, wherein the defined organic photoconductive compound is used in admixture with (an) other inorganic and/or organic photoconductive substance(s).

13. A process according to claim **12**, wherein the photoconductive compound is used in admixture with a photoconductive compound selected from the group of photoconductive selenium, and the photoconductive oxides, sulphides, and selenides, of zinc, cadmium, mercury, antimony, bismuth and lead.

14. A process according to claim **1**, wherein the photoconductive recording element has an optical density not higher than 0.30 for visible light or copying light.

15. A process according to claim **10**, wherein the recording element has been spectrally sensitized by means of a triarylmethane dye, a xanthene dye and/or a methine dye.

16. A recording material containing a photoconductive insulating recording element capable of being electrostatically charged in the absence of activating electromagnetic radiation and capable of retaining the applied charge for a period of time long enough to produce thereon a developed electrostatic charge pattern, characterized in that the recording element stands in electroconductive relationship to a layer or support with a lower resistivity than the recording element and in that the recording element contains an organic photoconductive compound corresponding to the following general formula:



wherein:

R represents a $(C_1$-$C_4)$ alkyl radical, and

Z_1 represents the necessary atoms to close an adjacent ring system of the fluorene series and a spectral sensitizing agent.

17. A recording material according to claim **16**, wherein R represents a methyl group.

18. A recording material according to claim **16**, wherein the recording element contains said organic photoconductive compound in a range of 10 percent – 75 percent by weight.

19. A recording material according to claim **16**, wherein the recording element is in layer or sheet form and stands in electroconductive contact with a layer or support that has a resistivity of at least 10^2 lower than that of the recording element in the dark.

20. A recording material according to claim **19**, wherein the support is a paper support.

21. A recording material according to claim **19**, wherein the support is an insulating transparent resin support coated with a transparent electroconductive interlayer.

22. A recording material according to claim **16**, wherein the photoconductive compound is used in admixture with a polymeric binding agent.

23. A recording material according to claim **22**, wherein the photoconductive compound is used in admixture with a halogen-containing polymer, an epoxy resin and/or a silicon resin.

24. A recording material according to claim **16**, wherein the photoconductive compound is used in admixture with an organic binding agent increasing the photosensitivity of the recording element.

25. A recording material according to claim **24**, wherein said spectral sensitizing agent is an organic dye.

26. A recording material according to claim **16**, wherein the photoconductive compound is used in admixture with (an) other inorganic and/or other organic photoconductive substance(s).

27. A recording material according to claim **26**, wherein the photoconductive compound is used in admixture with a photoconductive compound selected from the group of photoconductive selenium, and the photoconductive oxides, sulphides and selenides of zinc, cadmium, mercury, antimony, bismuth and lead.

28. A recording material according to claim **16**, wherein the photoconductive recording element has an optical density not higher than 0.30 for visible light or copying light.

29. A recording material according to claim **25**, wherein the recording element has been spectrally sensitized with a triarylmethane dye, xanthene dye and/or methine dye.

30. A recording material according to claim **29**, wherein the organic photoconductive compound is used in admixture with the spectrally sensitizing dye applied in an amount of 0.01 to 5.0 percent by weight in respect of said photoconductive compound.

31. A recording material according to claim **24**, wherein the recording element contains as chemical sensitizing agent a compound having (a) substituent(s) with strong electron-attracting (electro-negative) character.

32. A recording material according to claim **31**, wherein the chemical sensitizing agent is a non-ionic Lewis acid compound.

33. A recording material according to claim **32**, wherein the chemical sensitizing agent is a quinone containing halogen or cyano substituents.

* * * * *

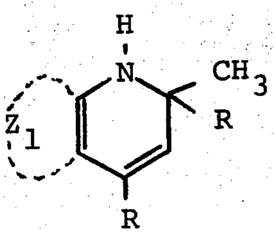
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,830,647 Dated August 20, 1974

Inventor(s) Wilhelmus JANSSENS et al

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

Column 19, Claim 1; Column 19, Claim 3; and Column 20, Claim 16, in the formula of each, correct the formula to read as follows: --



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Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents