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[54] **ORGANIC PHOTOCONDUCTORS SENSITIZED BY FREE RADICAL LIBERATORS AND ORGANOMETALLIC COMPOUNDS**

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Related U.S. Application Data

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[52] **U.S. Cl.** ..... **96/1.6**, 96/1.5, 96/90 R, 96/91 R, 96/92, 96/93, 96/75, 96/67, 96/74, 96/73

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

[58] **Field of Search** ..... 96/1 R, 1.5, 1.6, 35.1, 96/115 R, 115 P, 90 R; 204/159.24

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Primary Examiner—Roland E. Martin, Jr.

[57] **ABSTRACT**

A photosensitive material suitable for electrophotography is composed mainly of a free radical former capable of producing free radical by a radiation energy (F) and an organic photoconductive material (OPH) treated with a radiation energy in the presence of an organometallic compound (OM). If desired, a dye base compound or an organic colorization component may be added thereto. The photosensitive material may be produced by applying a radiation energy to a formulation containing F, OPH and OM.

40 Claims, No Drawings

ORGANIC PHOTOCONDUCTORS SENSITIZED BY FREE RADICAL LIBERATORS AND ORGANIMETALLIC COMPOUNDS

This is a continuation, of application Ser. No. 111,626, filed Feb. 1, 1971, now U.S. Pat. No. 3,765,883.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a photosensitive material and preparation of said photosensitive material. More particularly, this invention relates to photosensitive material mainly containing an organic photoconductive material and a free radical former capable of producing a free radical by exciting with a radiation energy subjected to a radiation energy in the presence of an organometallic compound and a method of producing said photosensitive material. This application is related to co-pending application Ser. No. 111,626 filed Feb. 1, 1971.

2. Description of the Prior Art

As electrostatic photographic photosensitive materials, there have been used metallic selenium and selen alloys for indirect electrostatic photography and metallic oxides such as zinc oxide for direct electrostatic photography, and they are widely used for reproduction apparatus. On the contrary, organic photoconductive materials are far better than selenium and zinc oxide in points of transparency, flexibility, light weight, film shapability, selectivity of charging polarity, and surface smoothness, but organic photoconductive materials have not been practically used for electrostatic photography. This is due to that the photosensitivity of organic photoconductive materials is remarkably lower than that of selenium and zinc oxide and, therefore, a strong light source is necessary for image-wise exposure after charging. As organic photoconductive materials, there have been known, for example, condensed polynuclear aromatic compounds such as anthracene, pyrene, perylene and the like, heterocyclic compounds such as triphenyl pyrazoline derivatives, acyl hydrazone derivatives and high polymers such as poly-N-vinylcarbazole. It has been recently contemplated to enhance the photosensitivity of the above mentioned conventional photoconductive materials of low sensitivity by using organic synthetic means. As the result, several useful photoconductive materials have been found. For example, they are brominated poly-N-vinylcarbazole disclosed in Japanese Patent Publication No. 25230/1967, poly-3,6-diiodo-9-vinylcarbazole disclosed in Japanese Patent Publication No. 7592/1968, poly-N-vinyl-3-aminocarbazole disclosed in Japanese Patent Publication No. 9639/1967, and polyvinylanthracene disclosed in Japanese Patent Publication No. 2629/1968. However, these photoconductive materials alone are not of high photosensitivity and therefore, they are used together with a spectral sensitizing dye for practical use. For example, a brominated polyvinylcarbazole is combined with a certain triaryl carbonium salt dye to give a photosensitivity comparable with that of zinc oxide sensitized by dye. As are clear from the above mentioned example, the organic photoconductive materials and the sensitizing dye combined therewith for sensitization are usually prepared by special and complicated organic syntheses and purification. Therefore, even if there is obtained high sensitivity, there remain economical and practical problems.

The prevent inventors have now found that organic photoconductive materials can be sensitized by a simple sensitizing treatment to give a high sensitivity comparable with or higher than that of conventional selenium or zinc oxide (dye-sensitized).

In a printing-out recording material known as free radical system, there is used a free radical former capable of producing free radical when excited by radiation energy, but such photosensitive material or recording material are low in stability. This is due to the free radical former used. For example, when as the free radical former, a polyhalogen compound such as carbon tetrabromide is employed, unreacted carbon tetrabromide is essentially present in a photosensitive layer of the photosensitive material or recording material and carbon tetrabromide is so volatile, unstable and poisonous that such photosensitive material or recording material can not be practically used.

According to the present invention it is possible to solve such drawbacks and provide a highly sensitive, economical and chemically stable photosensitive material for electrostatic photography.

SUMMARY OF THE INVENTION

The photosensitive material according to this invention is composed mainly of a free radical former capable of producing free radical by exciting with a radiation energy and an organic photoconductive material irradiated with a radiation energy in the presence of an organometallic compound.

According to another aspect of this invention, the photosensitive material may additionally contain a dye base compound and/or an organic colorization component.

According to a further aspect of this invention, the above mentioned photosensitive material may be prepared by applying a radiation energy, if desired, together with heat to the composition containing the above mentioned ingredients.

According to still another aspect of this invention, a photosensitive member may be produced by applying a radiation energy to the above mentioned ingredients present on a support.

An object of this invention is to provide an electrostatic photosensitive material highly sensitized and method for preparing the same.

Another object of this invention is to provide a highly sensitive organic photoconductive photosensitive material for electrostatic photography comprising a free radical former capable of producing free radical by a radiation energy and an organic photoconductive material subjected to a radiation energy in the presence of organometallic compound, and method for production thereof.

A further object of this invention is to provide an economical and highly sensitive organic photoconductive photosensitive material which is free from complicated organic syntheses and purification step and can be obtained by a simple sensitizing treatment, and method for production thereof.

Still another object of this invention is to provide a chemically stable and highly sensitive organic photosensitive material and method for production thereof.

DETAILED DESCRIPTION

Organic photoconductive materials used in this invention may be selected from the following wide material sources.

A. As vinylcarbazoles, there may be mentioned, for example, vinylcarbazole, poly-9-vinylcarbazole, 9-vinylcarbazole copolymer, 3-nitro-9-vinylcarbazole copolymer, 3-N-methylamino-9-vinylcarbazole copolymer, nitrated poly-9-vinylcarbazole, bromine substituted 9-vinylcarbazole copolymer such as 3-bromo-9-vinylcarbazole copolymer, brominated 9-vinylcarbazole copolymer and 3,6-dibromo-9-vinylcarbazole copolymer, poly-N-vinyl-3-aminocarbazole, bromine substituted poly-9-vinylcarbazole such as poly-3-bromo-9-vinylcarbazole, poly-3,6-dibromo-9-vinylcarbazole and brominated-N-vinylcarbazole, iodine substituted poly-9-vinylcarbazole such as 3-iodo-9-vinylcarbazole copolymer and poly-3,6-diiodo-9-vinylcarbazole, iodine substituted 9-vinylcarbazole copolymer such as 3-iodo-9-vinylcarbazole copolymer, poly-3-benzylideneamino-9-vinylcarbazole, α,ω-bis-(N-carbazole)-alkane derivative, vinylanthracene-N-vinylcarbazole copolymer, and 2- (or 3-) vinyl-9-alkyl carbazole homopolymer or copolymer wherein alkyl is primary alkyl group such as methyl, ethyl and propyl.

B. As aromatic amino derivatives, there may be mentioned, for example, aminopolyphenyl, allylideneazine, N,N′-diallyl-N,N′-dibenzyl phenylenediamine, N,N,N-′,N′-tetrabenzyl-p-phenylenediamine, N,N′-diphenyl-p-phenylenediamine, N,N′-dinaphthyl-p-phenylenediamine, and 4,4′-bisdimethylaminobenzophenone.

C. As diphenylmethanes and triphenylmethanes, there may be mentioned, for example, diphenylmethane dye leuco base and triphenylmethane dye leuco base.

D. As compounds having heterocyclic ring, there may be mentioned, for example, oxadiazole, 5-aminothiazole, 4,1,2-triazole, imidazolone, oxazole, imidazole, pyrazoline, imidazolidine, polyphenylene thiazole, 1,6-methoxyphenazine, and pyrazolinopyrazoline derivatives.

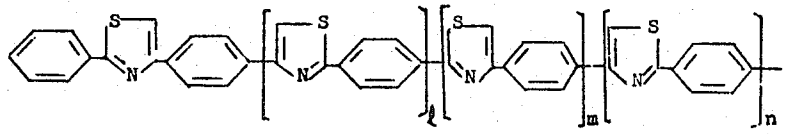
E. As compounds having a condensed ring, there may be mentioned, for example, benzthiazole, benzimidazole, benzoxazole derivatives such as 2-(4′-diaminophenyl)-benzoxazole, 2-(4′-dimethylaminophenyl)-benzoxazole, aminoacridine, quinoxaline, diphenylene hydrazone compound, pyrrocoline derivatives and 9,10-dihydroanthracene derivatives.

F. As compounds having a double bond, there may be mentioned, for example, acylhydrazone, ethylene derivatives, 1,1,6,6-tetraphenylhexatriene and 1,1,5-triphenyl-pent-1-ene-4-yn-3-ol.

G. As condensation products, there may be mentioned, for example, condensation product of aldehyde and aromatic amine, the reaction product of a secondary aromatic amine with an aromatic halide, and poly pyromethanoimido poly-p-phenylene-1,3,4-oxadiazole.

H. As vinyl polymers (excluding polyvinylcarbazole), there may be mentioned, for example, α-alkylacrylic acid amide polymer, polyvinylacridine, poly-[1,5-diphenyl-3-(4-vinylphenyl)-2-pyrazoline], poly(1,5-diphenyl)-pyrazoline, polyacenaphthylene, nuclear substituted polyacenaphthylene, polyvinylanthracene, and poly-2-vinyldibenzthiophene.

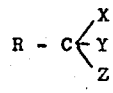
I. As organic photoconductive oligomers, there may be mentioned, for example, compound having the formula



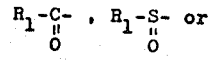
wherein *l*, *M* and *n* are each 0 or 1, and $l \geq m \geq N$. For example, as a five ring compound, there may be mentioned p-bis(2-phenyl-4-thiazolyl) benzene; as a seven ring compound, 2,4-bis[4-(2-phenyl-4-thiazolyl)-phenyl] thiazole; as a nine ring compound, 1,4-bis[4-{4-(2-phenyl-4-thiazolyl)-phenyl}thiazolyl]benzene.

Among these organic photoconductive materials, there are preferably used vinylcarbazole and its derivatives, aromatic amino derivative, and diphenylmethane and triphenylmethane derivatives. A free radical former employed in this invention is a material capable of producing a free radical by excitation with a radiation energy. A free radical former can be selected from the following classes of widely ranged substances.

A. As polyhalogen containing compounds, there may be used a compound of the general formula:



wherein R represents hydrogen, alkyl, halogen atom selected from Cl, Br and I,





wherein R_1 represents substituted or unsubstituted alkyl, aryl or heterocyclic group; X, Y and Z are similar or dissimilar, and hydrogen, alkyl or halogen atom selected from Cl, Br and I, at least one of X, Y and Z is halogen atom, for example, CBr_4, CI_4, CHI_3, C_2Cl_6, $CBrCl_3$, CCl_4, $CHBr_3$, $CHCl_3$, C_2Br_6, C_2HBr_5, $C_6H_5CBr_3$, $ClBr_3$, $ClCl_3$, $CHICl_2$, $CHIBr_2$, $CBrCl_3$, $CHBrCl_2$, 2,2,2-trichlorotoluene, 2,2,2-tribromo acetophenone, 1,1,1-tribromo-2-methyl-2-propanole, 1,1,2,2-tetra bromoethane, 2,2,2-tribromoethanole, CH_2Cl_2, CH_2Br_2, CH_2I_2, $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$, CH_3CHCl_2, CH_3CHBr_2, $CHCl_2CHCl_2$, $ClCH{=}CHCl$, $CHCl{=}CCl_2$, $Br(CH_2)_3Br$, $Br(CH_2)_4Br$, $Br(CH_2)_5Br$ and $Br(CH_2)_6Br$; halogenated organic sulfoxide such as pentabromodimethylsulfoxide and hexabromodimethylsulfoxide, halogenated organic sulfone compound such as hexabromodimethylsulfone, trichloromethyl-

phenyl sulfone, tribromomethylphenylsulfone, trichloromethyl-parachlorophenyl sulfone, tribromomethyl-paranitrophenyl sulfone, 2-trichloromethyl-benzoxathiazolyl sulfone, 4,6-dimethylpyrimidyl-2-tribromomethyl sulfone, tetrabromodimethyl sulfone, 2,4-dichlorophenyltrichloromethyl sulfone, 2-methyl-4-chlorophenyl trichloromethyl sulfone, 2,5-dimethyl-4-chlorophenyltrichloromethyl sulfone, 2,4-dichlorophenyl tribromomethyl sulfone, and bromomethyldibromomethylsulfone.

B. As carbonyl compounds, there may be mentioned, for example, vicinal polyketaldonyl compounds, α-carbonyl alcohols, acryloin ethers, α-hydrocarbon-substituted acryloins, polynuclear quinones.

C. As sulfur compounds, there may be mentioned, for example, alkyldisulfide, aralkyldisulfide, aryldisulfide, aroyldisulfide, acryldisulfide, cyclic alkyldisulfide, mercaptane, thiole, metalmercaptide, dithiocarbamates, O-alkylxanthene esters, and thiuram derivatives.

D. As a peroxide compound, there may be for example, hydroperoxide, dialkylperoxide, diacrylperoxide and diaroylperoxide.

E. As azo and diazo compounds, there may be mentioned, for example, azonitrile compound, diazo compound such as p-nitrobenzene diazonium-p-chlorobenzene sulfonate.

Among these free radical formers, a compound giving an especially excellent result is a polyhalogen containing compound.

The representative organometallic compounds used in this invention are alkylmetallic compound, arylmetallic compound, alkylarylmetallic compound and cyclopentadienyl-metallic compound. Metals in alkylmetallic compound, arylmetallic compound and alkylarylmetallic compound are metal elements in the Groups IVB and VB of the Periodic Table. The metals are preferably Ge, Sn, Pb, P, As, Sb and Bi. The metal in cyclopentadienyl compound is transition metal elements in the Groups IIIA, IVa, Va, VIA, VIIA and VIIIA. The transition metal elements as the Group IIIA element are Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb; as the Group IVA element Ti, Zr and Hf; as the Group VA element V, Nd and Ta; as the Group VIA element Cr, Mo, W and U; as the Group VIIA element Mn, Tc and Re; and as the Group VIIIA element Fe, Co, Ni and Ru.

The examples for these organometallic compound are the followings.

As the alkylmetallic compound, arylmetallic compound and alkylarylmetallic compound, there may be mentioned, for example, triphenylmetallic compound such as triphenyl bismuthine, triphenylstibine, triphenylarsine and triphenylphosphine, tetraphenylmetallic compound such as tetraphenyldistibine, tetraphenyllead, tetraphenyltin, tetraphenylarsine and tetraphenylgermanium, benzyltriphenyllead, trimethyltriphenylditin, hexamethylditin and hexaphenylditin. The alkyl group, aryl group or alkylaryl group is attached to the metal element so as to satisfy the valency of the metal element to form a metal — carbon bond. As organometallic compounds having the Group IIIA element, there may be mentioned, for example, cyclopentadienyl compounds of candium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium and ytterbium. As an organometallic compound having the Group IVA transition elements, there may be mentioned, for example, bis (cyclopentadienyl) titanium, dihalogenated bis(cyclopentadienyl) titanium, bis (cyclopentadienyl) titanium diaryl, and bis (cyclopentadienyl) zirconium dibromide.

As an organometallic compound having the Group VA transition element, there may be mentioned, for example, bis (cyclopentadienyl) vanadium dihalide, bis (cyclopentadienyl) niobium tribromide, bis (cyclopentadienyl) tantalum tribromide, bis (cyclopentadienyl) vanadium, and cyclopentadienyl vanadium tetracarbonyl.

As an organometallic compound having the Group VIA transition element, there may be mentioned, for example, bis (cyclopentadienyl) chromium, bis (cyclopentadienyl)- μ-pentacarbomonooxide-bimolybdenum, bis (cyclopentadienyl)- μ-hexacarbon-monooxide-bitungsten, tris (cyclopentadienyl) uranium chloride.

As an organometallic compound having the Group VIIA transition element, there may be mentioned, for example, bis (cyclopentadienyl) manganese, and hydrogenated bis (cyclopentadienyl) rhenium.

As an organometallic compound having the Group VIIIA transition element, there may be mentioned, for example, bis (cyclopentadienyl) iron [ferrocene], bis (cyclopentadienyl) iron dicarbonyl, cyclopentadienyliron dicarbonyl chloride, cyclopentadienylirondicarbonyl cyanate, bis (cyclopentadienyl) cobalt bromide, bis (cyclopentadienyl cobalt [cobaltocene], cyclopentadienyl cobalt dicarbonyl, bis (cyclopentadienyl) nickel [nickelocene], cyclopentadienylnickelnitrosyl, bis (cyclopentadienyl) ruthenium and bis (cyclopentadienyl) ruthenate.

One or more of the organometallic compounds may be used. Among the above-mentioned organometallic compounds, there are preferably used triphenylbismuthine, triphenylphosphine, tetraphenylallene, ferrocene and cobaltocene.

The radiation energy source used in this invention is selected depending upon organometallic compounds, free radical formers, organic photoconductive materials and/or solvent used. Any kind of light source may be used as far as it can produce free radical from a free radical former in the sensitization system. Preferably a light source emitting a large amount of ultraviolet ray or near ultraviolet ray such as mercury (low pressure, high pressure or super high pressure), metal halide lamp and xenon lamp is used. If desired, a radiation energy such as ultraviolet ray can be applied together with heat to accelerate the decomposition of free radical formers by selecting the temperature at which the radiation energy is applied and the time of irradiation in such a manner that there are balanced the degree of sensitization and undesirable secondary effects such as remarkable colorization and gellation. Furthermore, it is clear that the decomposition of free radical former and the accompanying chemical reaction can be controlled by adjusting the time of applying the radiation energy. The effective wave length of radiation energy is, for example, illustrated below.

Halogen compound	300 – 400 mμ
Carbonyl compound	360 – 380 mμ
Organic sulfur compound	280 – 400 mμ
Peroxide	300 – 400 mμ
Azo compound	340 – 400 mμ

Among them, effective wave length for some halogen compounds is shown below.

CBr_4	lower than	400 mμ
$CHBr_3$, CH_2Br_2	do.	330 do.
$CBrCl_3$	do.	400 do.
CHI_3	do.	400 do.

The sensitization treatment may be effected as follows. An organic photoconductive material, a free radical former and an organometallic compound are brought into coexistence to form a uniform solution by using an appropriate solvent and a radiation energy is applied to the resulting solution for sensitization treatment. In this case, if an organometallic compound is not used, it is very difficult to select an appropriate solvent since the solvent should have a sufficient solubility to the organic photoconductive material and the free radical former, and furthermore such a solvent which reduces the sensitization effect should be avoided. For example, in case of using poly-N-vinylcarbazole as organic photoconductive material and carbon tetrabromide as free radical former, benzene and monochlorobenzene can enhance the sensitization effect while tetrahydrofuran and dioxane reduce the sensitization effect.

The present inventors have found that the reduction of sensitization effect caused by solvent is remarkably weakened by incorporating a small amount of an organometallic compound in the reaction system. For example, there may be used methylene chloride, chloroform, toluene and xylene which are usually not preferable, and further tetrahydrofuran and dioxane which are extremely unfavorable can also be sufficiently used. Thus the selection range of solvent is very broadened.

The use of organometallic compound results in high sensitivity. The sensitizing effect of the organometallic compounds is illustrated in the Examples appearing later. When a solution containing a free radical former and an organic photoconductive material has a color or the solution contains additionally a dye base compound or an organic colorization component, the sensitization effect can be visually observed since the colorization of the solution is markedly accelerated.

The sensitization treatment may be carried out by various methods such as, for example, applying a radiation energy to a solution comprising an organometallic compound and a free radical former followed by mixing with a solution of an organic photoconductive solution, or applying a radiation energy to each of a solution containing a free radical former and an organic photoconductive material and a solution containing a free radical former and an organometallic compound followed by mixing these two solutions, or applying a radiation energy to a solution containing an organic photoconductive material, a free radical former and an organometallic compound coated on a base support. Furthermore, a photosensitive material of higher sensitivity can be obtained by additionally incorporating a dye base compound or organic colorization component thereto. Particularly, in case of applying a radiation energy to a solution containing an organic photoconductive material, a free radical former, an organometallic compound and, if desired, a dye base compound and/or an organic colorization component which is coated on a base support, any solvent can be selected as far as the solvent can dissolve the organic photoconductive material. This free selection of solvent is very valuable.

The change caused by applying a radiation energy to organic photoconductive material, free radical former and organometallic compound is considered to occur in the following sequence.

Assuming that the free radical former is a polyhalogen compound of the formula

$$R - CX_3$$

where R is hydrogen, halogen, alkyl or aryl (substituted or unsubstituted) and each X may be, the same or different, chlorine, bromine or iodine, when the polyhalogen compound is exposed to a sufficient amount of radiation energy, the following reaction proceeds:

$$R{-}CX_3 \rightarrow R{-}\dot{C}X_2 + X\cdot \qquad (1)$$

The X thus formed (halogen free radical) extracts hydrogen from a medium to form secondarily HX (halogen acid) as follows.

$$X\cdot \xrightarrow{H} HX \qquad (2)$$

the $R{-}CX_2$ (organic free radical) is considered as a chain carrier causing reactions (1) and (2) above as chain reaction.

When an organometallic compound (M) is present in the reaction system, the radical formation efficiency by a radiation energy is increased as shown in the following formula:

$$R{-}CX_3 \xrightarrow{m} R{-}\dot{C}X_2 + X\cdot \qquad (3)$$

It is considered that the organometallic compound works as a reaction accelerator or catalyst.

Therefore, the reactions shown in Formulas (1) and (2) can be effectively caused and the reaction time is shortened by the action of the organometallic compound and simultaneously the reaction conditions such as selectivity of solvent, tolerable amounts of impurity, and temperature range for reactions of Formulas (1) and (2) can be broadened. And further the addition of organometallic compound results in improvement in photosensitivity.

According to the present invention, the above-mentioned organometallic compound and halogen compound are added to a solution of organic photoconductive material and the resulting solution is subjected to a radiation energy sufficient to cause the reactions in Formulas (1) and (2) to sensitize remarkably the organic photoconductive material. It has now been found that the above mentioned sensitizing treatment can improve photosensitivity of photosensitive materials for electrophotography, but the mechanism of sensitization is not yet fully understood. The amount of the free radical former used in this invention is appropriately selected depending upon each particular photoconductive material and amount of radiation energy. In general, the amount of the free radical former is preferably 1 – 30 percent by weight. The amount of organometallic compound used in this invention is appropriately selected depending upon each particular photoconductive material, free radical former, and amount of radiation energy. In general, the amount of the organometallic compound preferably ranges from 10^{-3} to 10 percent by weight.

When the organic photoconductive material itself has film shapability, it is not necessary to use a binder resin or plasticizer, but when it lacks in film shapability, it is desirable to use a binder resin of 30 – 100 percent

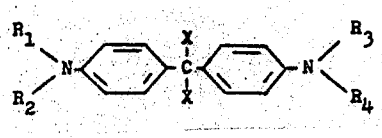
by weight based on the photoconductive material. For the purpose of improving the property of film, 5 – 100 percent by weight plasticizer may be added. Representative binder resins are polystyrene resin, polyvinyl chloride resin, phenolic resin, polyvinyl acetate resin, polyvinyl acetal resin, epoxy resin, xylene resin, alkyd resin, polycarbonate resin and acrylonitrile-styrene resin.

Representative plasticizers are dioctylphthalate, tricresylphosphate, diphenyl chloride, methyl naphthalene, p-terphenyl and diphenyl.

In order to further enhance photosensitivity of the photosensitive material for electrography obtained by this invention and adjust the spectral sensitivity characteristics, it is effective to add a dye sensitizer or Lwiss acid usually used in electrophotography singly or in combination. Furthermore, it is also effective for increasing photosensitivity of the photosensitive material to add a dye base compound capable of forming a coloring matter by the reaction with a free radical former caused by a radiation energy. In addition, it is effective to add an organic colorization component capable of forming a coloring material by the reaction with a free radical former caused by a radiation energy. These dye base compound and organic colorization components can produce a far higher sensitization effect than that obtained by usual dye sensitizer.

Representative dye base compounds are shown below.

As leuco base or carbinol base, there may be mentioned, for example, leuco base of triphenylmethane dye such as leuco malachite green, leuco crystal violet, leuco methylviolet, leuco opal blue; carbinol base of triphenylmethane dye such as carbinol crystalviolet, carbinol methylviolet, leuco base or carbinol base of diphenylmethane dye having the formula



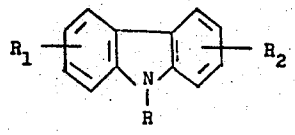
where R_1, R_2, R_3 and R_4 represents a member selected from the group consisting of hydrogen, alkyl, aralkyl and aryl (substituted or unsubstituted), when X is —H, leuco base, when X is —OH, carbinol base; such as Michler's hydrol, styryl dye such as 4-(4-dimethylaminophenyl-1,3-butadienyl)-quinoline, 4-p-dimethylaminostyrylquinoline, 2-p-dimethylaminostyrylquinoline and 2-p-dimethylaminostyrylquinoline, cyanine dye such as 2-[3-ethyl-2(1H)-quinolylidenepropenyl] quinoline, 2-[2-methyl-3-(3-ethyl-2(3H)-benzothiazolylidene)-propenyl]benzothiazole, 4-[2-(3-ethyl-2(3H)-benzothiazolylideneamino) vinyl]quinoline, 4-(1-ethyl-2(1H)-quinolyldeneamino)quinone, 2-(p-dimethylaminobenzylidene) aminoquinoline, and 4-(p-dimethylaminophenylimino)-cyanomethylquinoline, merocyamine dye base such as 3-ethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene] rhodanine, 1-ethyl-3-[(3-ethyl-2(3H)-benzoxazolylidene]-oxyindole, and 4-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylindene]-3-phenyl-5(4H)-isooxazolone, leuco dihydroanthracene compound such as 2,7-bis(dimethylamino)-10-p-dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene and 2,7-bis(dimethylamino) 9,10-dihydro-9,9-dimethylanthracene. There may be mentioned the following compounds as organic colorization components used in this invention.

As an arylamines there may be mentioned, for example, a compound of the general formula:



wherein R represents a member selected from the group consisting of hydrogen, alkyl, aryl and aralkyl (substituted or unsubstituted), R_1 represents a member selected from the group consisting of phenyl, α-naphthyl and β-naphthyl; R_2 represents a member selected from the group consisting of alkyl, aryl and aralkyl (substituted or unsubstituted), such as diphenylamino, N-methylaniline, N,N-dimethylaniline, N-ethylaniline, N,N-diethylaniline, phenyl-α-naphthylamine, phenyl-β-naphthylamine, triphenylamine and N-methyldiphenylamine.

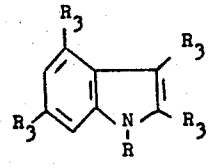
B. Carbazoles have the general formula:



wherein R represents a member selected from the group consisting of hydrogen, alkyl, alkenyl, aralkyl and aryl (substituted or unsubstituted), R_1 and R_2 are similar or dissimilar, a member selected from the group consisting of hydrogen, alkyl, alkenyl, aralkyl, alkoxy, halogen and dialkylamino.

As such a compound there may be mentioned, for example, carbazole, N-ethylcarbazole, N-methylcarbazole, N-phenylcarbazole, N-benzylcarbazole, N-vinylcarbazole, 3,6-dibromo-N-vinylcarbazole, 3-chloro-N-ethylcarbazole, 3-chloro-N-vinylcarbazole, 3-iodo-N-vinylcarbazole and 3-dimethylamino-N-ethylcarbazole.

C. Indoles having the general formula:



wherein R represents a member selected from the group consisting of hydrogen, alkyl, aralkyl and aryl (substituted or unsubstituted), each of R_3 is similar or dissimilar, a member selected from the group consisting of hydrogen, alkyl, alkoxy, halogen and dialkylamino.

As such a compound, there may be mentioned, for example, indole, 2-methylindole, 1,2-dimethylindole, 1-phenylindole, 4-chloroindole and N-vinylindole.

D. As a 1,3,4-oxathiazoles, there may be mentioned, for example, 2,5-bis-[4'-dimethylaminophenyl-1']-1,3,4-oxadiazole, 2,5-bis-[4'-diethylaminophenyl-1']-1,3,4-oxadiazole, 2,5-bis-[4'-n-propylaminophenyl-1']-1,3,4-oxadiazole and 2,5-bis-[4'-cyclohexylaminophenyl-1']-1,3,4-oxadiazole.

E. As 1,3,4-triazoles, there may be mentioned, for example, 1-methyl-2,5-bis-[4'-N,N-diethylaminophenyl-

1']-1,3,4-triazole, 2,5-bis-[4'-N,N-diethylaminophenyl-1']-1,3,4-triazole, 2,5-bis-[4'-aminophenyl-1']-1,3,4-triazole and 2,5-bis-[4'-N-ethylaminophenyl-1']-1,3,4-triazole.

E. As imidazoles there may be mentioned, for example, 4-(4'-dimethylaminophenyl)-5-(4''-chlorphenyl)-imidazole, 1-methyl-2-(diethylaminophenyl)-4,5-diphenyl-imidazole, 4-(4'-dimethylaminophenyl)-5-phenyl-imidazole and 2-(4'-dimethylaminophenyl)-4,5-diphenyl-imidazole.

G. As pyrazolines, there may be mentioned, for example, 1,3,5-triphenylpyrazoline, 1,5-diphenyl-3-styrylpyrazoline, 1,3-diphenyl-5-p-oxyphenyl-pyrazoline, and 1 -phenyl-3-p-dimethylaminostyryl-5-p-dimethylaminophenylpyrazoline.

H. As aminophenyl substituted oxazoles, there may be mentioned, for example, 2-(4'-dimethylaminophenyl)-4-(4'-dimethylaminophenyl)-5-(2'-chlorphenyl)-oxazole, 2-(4'-dimethylaminophenyl)-4-(4'-dimethylaminophenyl)-5-phenyl-oxazole, and 2-(2'-chlorphenyl)-4-(4'-dimethylaminophenyl)-5-(2'-chlorphenyl)-oxazole.

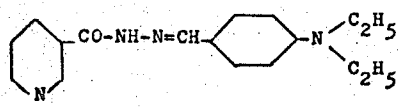
I. As benzidine compounds, there may be mentioned, for example, ortho-tridine, N,N'-diphenylbenzidine, naphthdidine, and benzidine.

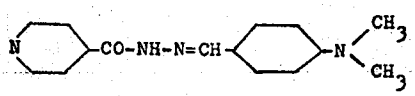
J. As 1,3-diphenyl-tetrahydroimidazoles, there may be mentioned, for example, 1,3-diphenyl-2-(4'-dimethylaminophenyl)-tetrahydroimidazole, 1,3-diphenyl-2-styryltetrahydroimidazole and 1,3-diphenyl-2-styryltetrahydroimidazole.

K. As phenazine compounds, there may be mentioned, for example, 1,6-dimethoxyphenazine, and 1,6-dimethylphenazine.

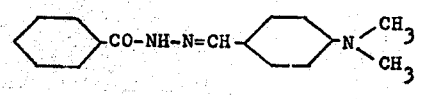
L. As acridine compounds, there may be mentioned, for example, 3,6-bis(diamino)acridine, 3,6-bis(dimethylamino)-acridine and acridine.

M. As acylhydrazone derivatives, there may be mentioned, for example, compounds having the formulae





and

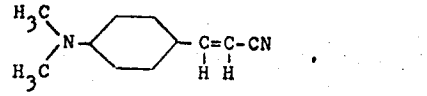


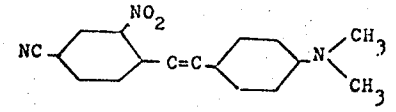
N. As quinoxaline compounds there may be mentioned, for example, 2,3-bis-(4'-methoxyphenyl)-6-aminoquinoxaline, 2-phenyl-3-(4'-dimethylaminophenyl)-6-chloroquinoxaline, and 2-phenyl-3-(4'-dimethylaminophenyl)-6,7-benzoquinoxaline.

O. As arylideneazine compounds containing N-disubstituted-amino group, there may be mentioned, for example, bis-4,4-diallyl-aminobenzylideneazine, bis-4,4-diethylamino-2,2-dimethylbenzylideneazine, bis-4,4-dibenzylaminobenzylideneazine, and bis-4,4-arylmethylaminobenzylideneazine.

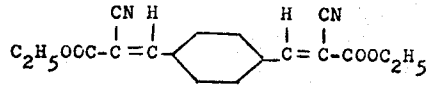
P. As pyridine and quinoline compounds, there may be mentioned, for example, 2-[1,3-dioxohydrindenyl-(2)]quinoline, 2-[4-chlor-1,3-dioxohydrindenyl-(2)]quinoline, 2-[1,3-dioxohydrindenyl-(2)]pyridine, and 4-methyl-2-[1,3-dioxohydrindenyl-(2)]pyridine.

Q. As ethylene derivatives, there may be mentioned, for example, compounds having the formulae





and



R. As spiropyrans, there may be mentioned, for example, 1,3,3-trimethylindolinobenzopyrylspiran, 1,3,3-trimethylindolino-6'-nitrobenzopyrylspiran, 1,3,3-trimethylindolino-6'-nitro-8'-methoxybenzopyrylspiran and 1,3,3-trimethylindolino-6'-methoxy-8'-nitrobenzopyrylspiran.

According to the present invention, a photosensitive material may be prepared by applying a radiation energy simultaneously with heat to a free radical former capable of producing free radical by a radiation energy and an organic photoconductive material in the presence of an organometallic compound; or applying a radiation energy to a solution system containing a free radical former capable of producing free radical by a radiation energy, an organic photoconductive material and an organometallic compound; or applying a radiation energy to a solution system containing a free radical former capable of producing free radical by a radiation energy and an organometallic compound and mixing the solution system thus treated with a solution system containing at least an organic photoconductive material; or mixing a solution system containing a free radical former capable of producing free radical by a radiation energy, an organic photoconductive material and an organometallic compound irradiated by a radiation energy with a solution system containing a free radical former and, if desired, additionally an organometallic compound irradiated by a radiation energy.

In the above preparation methods, a dye base compound and/or an organic colorization components may be added to the system.

According to a method of producing a photosensitive member of this invention, a solution containing an organic photoconductive material, a free radical former

and an organometallic compound subjected to or to be subjected to a sensitizing treatment by using a radiation energy may be applied to a transparent or opaque support by conventional coating methods such as roll coating method, wire-bar coating method, air-knife method and the like. The radiation energy may be applied to the solution before or after the solution is coated on a support. For example, a radiation energy is applied to the solution coating while the coating is being continuously formed followed by drying. Furthermore, if desired, a dye base compound or an organic ccolorization component may be added at this stage.

The method of producing a photosensitive member according to this invention is simple and of high efficiency.

Some examples of this production of photosensitive member are shown below.

1. A formulation solution mainly containing an organometallic compound, an organic photoconductive material and a free radical former is coated on a support and then irradiated by a radiation energy sufficient to cause a remarkable sensitization in the resulting coating layer.
2. The formulation solution as in item (1) above is coated on a support, subjected to a radiation energy sufficient to cause a remarkable sensitization in the resulting coating layer and dried while the sensitization in the coating layer is accelerated.
3. The formulation solution as in item (1) above is coated on a support and simultaneously photo energy and thermal energy are applied to the coating.
4. The formulation solution as in item (1) above is coated on a support and simultaneously photo energy and thermal energy are applied to the coating, and then the resulting coating is dried by a thermal energy.

The thickness of the resulting photoconductive layer on the support may be adjusted to a range of from several microns to several tens microns. For usual purposes, it is less than 10 microns and several microns.

As the support, there may be used metal sheet such as aluminum, copper, zinc and silver, paper treated in such a manner that a solvent does not permeate, aluminum laminate paper, synthetic resin film in which a surfactant is incorporated, glass on which surface a metal, metal oxide or metal halide is deposited by the vapor-deposition, paper and synthetic resin films such as polyethylene, polypropylene, polyethylene terephthalate, polystyrene, polyvinyl chloride, ethyl cellulose, cellulose acetate and polyester. In general, any support having a surface resistivity lower than that of the photoconductive layer may be used. In other words, such material having a resistivity of lower than $10^9\Omega$, preferably lower than $10^5\Omega$ may be used.

All known technique of conventional electrophotographic processes may be employed. There may be generally used a Carlson process comprising charging, exposing, developing and fixing steps. For example, positive charge is accumulated and its potential reaches 150–600 V. by passing the photosensitive member below the corona discharger charged with +6 KV in the dark several times. Then, from an appropriate light source such as a tungsten lamp, light is projected through an adequate positive pattern, then the electric charge at the exposed region is neutralized. Then, the latent image thus formed is developed with a negatively charged toner by, for example, a magnet brush developing method, cascade developing method or a fur-brush developing method to produce the positive image. This image may be fixed by heating or passing it through an appropriate solvent vapor. Liquid developing method may also be used. In this case, althrough the liquid developer as necessary constituents a coloring component and a carrier liquid, it is possible to add to it a controlling agent and an agent improving fixing property when desired. Further, the electric charge applied by corona charging may be a positive charge or a negative charge.

The following examples are given for illustrating the present invention, but should not be construed as limitation.

Example 1

Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by Badische Anilin und Soda Fabrik)	8 g.
Carbon tetrabromide	400 mg.
Triphenylbismutin	8 mg.
Benzene	200 ml.

To a solution comprising the above ingredients was applied a light irradiation for 5 minutes by using a photochemical reactor having a 100 watt high pressure mercury lamp produced by Ushio Denki Kabushiki Kaisha (When the solution excluding triphenylbismutin is used, the irradiation time for producing the same photosensitivity was as long as 15 minutes.). The solution thus treated was applied, in an amount of about 5 g/m^2 as solid matter, to a base paper (70 g/m^2) subjected to a solvent permeation inhibiting treatment by coating polyvinyl in an amount of about 2 g/m^2, and then dried for 5 minutes to form a photosensitive paper. Then the resulting photosensitive paper was given an uniform negative charge of about 380 V by corona charging using a charging apparatus of about 5.5 KV, contacted with an original positive film, exposed to a 150 watt tungsten lamp at 100 lux.sec, and soaked in a liquid developer for positive image to produce positive images of high fidelity to the original image.

When a solution not containing triphenylbismutin was employed, the required exposure amount was about 250 lux.sec.

When the solution containing the above-mentioned ingredients was coated on the above-mentioned base paper and irradiated with a high pressure mercury lamp of 100 watt at a distance of 150 mm for 5 seconds, the resulting photosensitive paper also gave a positive image of high fidelity to the original image under the reproduction conditions similar to the above ones while 30 seconds irradiation was necessary to give the same photosensitivity when the solution excluding triphenylbismutin was employed.

In the instant Example, the sensitization effect by triphenylbismutin was able to be measured by the degree of colorization of the solution caused by the light irradiation. That is, when triphenylbismutin is present, the solution was colorized to bluish by the light irradiation for 5 minutes while it took 15 minutes to colorize to bluish in the absence of triphenylbismutin.

When a poly-9-vinylcarbazole obtained by precipitation purification of the poly-9-vinylcarbazole as mentioned in the above formulation or obtained by precipitation purification of a poly-9-vinylcarbazole obtained

by polymerizing vinylcarbazole was employed in place of Luvican M-170 in the instant Example, a 5 minute irradiation can colorize the solution to bluish while blue colorization was hardly observed and a lowering of photosensitivity was observed with 5 minute irradiation when the solution excluding triphenylbismutin.

When 80 mg. of lenco malachite green was added to the above-mentioned formulation and irradiated for 2 minutes, the exposure amount producing clear positive images for the resulting photosensitive paper was 95 lux.sec.

When 200 mg. of N-vinylcarbazole was added to the above-mentioned formulation and irradiated for 5 minutes, the exposure amount producing clear positive image for the resulting photosensitive paper was 90 lux.sec.

For reference, a photosensitive paper obtained by coating a solution of poly-9-vinylcarbazole above requires an exposure amount of about 60,000 lux.sec. for producing good positive images. A commercially available dye-sensitized zinc oxide photosensitive paper requires about 95 lux.sec. to produce good positive images.

Example 2

Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by Badische Anilin und Soda Fabrik, hereinafter called "BASF")	4 g.
Acrylonitrile-styrene copolymer (Estylene AS-6INT, trade name, supplied by Yahata Kagaku)	4 g.
Carbon tetrabromide	400 mg.
Triphenylbismutin	16 mg.
Methylene chloride	200 ml.

A mixture of the above-mentioned ingredients was used to produce a photosensitive paper in a way similar to Example 1, the light irradiation being effected for 5 minutes. The resulting photosensitive paper was given a uniform negative charge of about 380 V by corona charging by using a charging apparatus of about 5.5 KV, contacted with an original positive film, exposed to a 150 watt tungsten lamp at 200 lux.sec., and soaked in a positive liquid developer to produce clear positive images of high fidelity to the original image.

Following the instant Example except that 400 mg. of tribromomethylsulfone was used in place of carbon tetrabromide and 50 mg. of leuco crystal violet was employed as a dye base compound, an exposure amount for obtaining clear positive images was 190 lux.sec. Further, when 80 mg. of N-methyldiphenylamine was added as an organic colorization component in place of leuco crystal violet in the above procedure, the exposure amount for producing clear images was 180 lux.-sec.

Example 3

Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by BASF)	8 g.
Carbon tetrabromide	400 mg.
Bis (cyclopentadienyl) titanium diphenyl	8 mg.
Benzene	200 ml.

The mixture of the above-mentioned ingredients was irradiated in a manner similar to Example 1. Then, 5 ml. of a solution of 80 mg. of 1, 3, 5-trinitrobenzene in benzene was added thereto as Lewis acid. Then, following the procedure of Example 1, there was produced a photosensitive paper. The resulting photosensitive paper was given a uniform negative charge of about 350 V by corona charging using a charging device of about 5.5 KV, contacted with an original positive film, exposed to a 150 watt tungsten lamp at 120 lux.sec., and soaked in a positive liquid developer to form clear positive images of high fidelity to the original positive image.

Example 4

Poly-9-vinylcarbazole (P0-098, trade name, supplied by Schuchardt)	2 g.
Tribromomethylphenylsulfone	100 mg.
Triphenylbismutin	2 mg.
Dioctylphthalate	0.5 g.
Chlorobenzene	70 ml.

A solution composed of the above ingredients was coated on a base paper of 79 g/m², which was treated with a hydrophilic polymer so as to inhibit the permeation of a solvent, in an amount of about 5 g/m² by a double roll coating method and, after coating is finished, the resulting coating was immediately irradiated by a 500 watt xenon lamp at a distance of about 10 cm for 5 seconds to produce a photosensitive paper. When triphenylbismutin was not used, the required irradiation time was 15 seconds. The resulting photosensitive paper was given a uniform negative charge of about 280 V by corona charging by using a charging device of about 5.5 KV, placed under an original positive film, exposed to a 15 watt tungsten lamp at 150 lux.sec., and soaked in a positive liquid developer to produce a positive image of high fidelity to the original image.

In the following Examples 5 – 39 the procedures follow Example 1. That is, a solution obtained by mixing the listed ingredients is irradiated with a 100 watt high pressure mercury lamp for 5 minutes, coated on a base paper, and dried to produce a photosensitive paper. The resulting photosensitive paper is subjected to corona charging by a charging device of about 5.5 KV, contacted with an original positive film and exposed to a 150 watt tungsten lamp.

In each of Examples 5 – 39 there are shown a formulation for the solution, an exposure amount necessary for obtaining clear positive images and, for comparison, an exposure amount necessary for obtaining clear positive images when the organometallic compound is not employed.

Example 5

Poly-3-bromo-9-vinylcarbazole	8 g.
Di-tertiarybutyl-P-oxide	400 mg.
2,7-Bis (dimethylamino)-10-P-dimethyl aminophenyl-9, 10-dihydro-9, 9-dimethyl Anthracene	100 mg.
triphenylphosphine	8 mg.
Monochlorbenzene	200 ml.

The exposure amount needed 170 lux.sec. When triphenylphosphine was not contained, the exposure amount was 350 lux.sec.

Example 6

Copolymer of 3-iodo-9-vinylcarbazole and	

Example 6-Continued

9-vinylcarbazole (in ratio of 40 : 60)	8 g
Bromoform	400 mg.
1,2-Dimethylindole	100 mg.
Triphenylphosphine	8 mg.
Benzene	200 ml.

The exposure amount needed 160 lux.sec. However, when triphenylphosphine was not contained, the exposure amount was 390 lux.sec.

Example 7

Poly-9-vinylcarbazole (PC-098 trade name, supplied by Schuchardt Co.)	8 g.
Carbon tetrabromide	400 mg.
Triphenylbismuthine	8 mg.
Benzene	200 ml.
Orient pink	20 mg.

The exposure amount needed 90 lux.sec. However, when triphenylbismuthine was not contained, the exposure amount was 300 lux.sec.

Example 8

Poly-3-bromo-9-vinylcarbazole	8 g.
Tribromomethylphenylsulfone	400 mg.
2-[1,3-Dioxo-hydrinedenyl-(2)] quinoline	50 mg.
Cobaltocene	0.5 mg.
Monochlorbenzene	200 ml.
Methyl violet	20 mg.

The exposure amount needed 80 lux.sec. When cobaltcene was not contained, the exposure amount was 280 lux.sec.

Example 9

Graft-copolymer of 9-vinylcarbazole and ethylacrylate	8 g.
Bromoform	400 mg.
Leuco methylviolet	80 mg.
Cobaltcene	0.5 mg.
Toluene	200 ml.
Diphenyl chloride	2 g.
2, 4, 7-Trinitro-9-fluorenone	50 mg.

The exposure amount needed 140 lux.sec. When cobaltcene was not contained, the exposure amount was 325 lux.sec.

Example 10

Poly-3-bromo-9-vinylcarbazole	8 g.
Carbon tetrabromide	400 mg.
Triphenylbismuthine	8 mg.
Benzene	200 ml.
P-ter-phenyl	4 g.

The exposure amount needed 95 lux.sec. When triphenylbismuthine was not contained, the exposure amount was 280 lux.sec.

Example 11

Poly-9-vinylcarbazole (trade name Luvican M-170 supplied by BASF)	8 g.
Carbon tetrabromide	400 mg.
4- (P-dimethylaminostyryl) quinoline	80 mg.
Tetraphenyllead	8 mg.
Benzene	200 ml.

The exposure amount needed 90 lux.sec. When tetraphenyllead was not contained, the exposure amount was 255 lux.sec.

Example 12

Graft-copolymer of 9-vinylcarbazole and ethylacrylate (in the ratio of 90 : 10)	8 g.
Carbon tetrabromide	200 mg.
N-vinylcarbazole	800 mg.
Bis (cyclopentadienyl) - zirconium dibromide	8 mg.
Benzene	200 ml.
Diphenyl chloride	2 g.
2, 4, 7-trinitro-9-fluorenone	50 mg.

The exposure amount needed 185 lux.sec. When bis (cyclopentadienyl) zirconium dibromide was not contained, the exposure amount was 395 lux.sec.

Example 13

Copolymer of 3-iodo-9-vinylcarbazole and 9-vinylcarbazole (in the molar ratio of 40 : 60)	8 g.
Iodoform	400 mg.
Triphenyl bismuthine	4 mg.
Benzene	200 ml.

The exposure amount needed 70 lux.sec. When triphenyl bismuthine was not contained the exposure amount was 250 lux.sec.

Example 14

Bis- 4, 4'-dialkylaminobenzylideneazine	4 g.
Copolymer of acrylonitrile and styrene (trade name Estylene AS-61NT supplied by Yahata Kagaku)	4 g.
Pentabromodimethylsulfoxide	400 mg.
4-[2- (3-ethyl-2(3H)-benzothiazolylideneamino) vinyl] quinoline	80 mg.
Ferrocene	0.1 mg.
Methylene chloride	200 ml.
Acridine yellow	20 mg.
Chloranil	70 mg.

The exposure amount needed 380 lux.sec. When ferrocene was not contained, the exposure amount was 140 lux.sec.

Example 15

Nitrated poly-9-vinylcarbazole (having 0.06 molars of nitro radical per one carbazole unit mainly at 3-position of carbazole ring)	8 g.
Iodoform	100 mg.
2.5-Bis- [4'-dimethylaminophenyl-1'] -1, 3, 4-oxadiazole	100 mg.
Triphenylarsine	8 mg.
Benzene	200 ml.

The exposure amount needed 275 lux.sec. When triphenylarsine was not contained, the exposure amount was 560 lux.sec.

Example 16

Poly-3-bromo-9-vinylcarbazole	8 g.
Iodoform	400 mg.

Example 16-Continued

Triphenylphosphine	8 mg.
Nitrobenzene	200 ml.
Methylviolet	20 mg.

The exposure amount needed 155 lux.sec. When triphenylphosphine was not contained, the exposure amount was 335 lux.sec.

Example 17

Poly-9-vinylcarbazole (trade name Luvican M-170 supplied by BASF)	8 g.
Carbon tetrabromide	400 mg.
1- Methyl-2,5-bis 4'-N,N'-diethylaminophenyl-1'-1, 3, 4-Triazole	80 mg.
Nickelocene	0.5 mg.
Benzene	200 ml.

The exposure amount needed 105 lux.sec. When nickelocene was not contained, the exposure amount was 210 lux.sec.

Example 18

Bis-4,4-diallylaminobenzylidenazine	4 g.
Modified phenol resin (trade name Beckacite 1100 supplied by Japan Reichhold Chemical Ind. Co.)	4 g.
Iodoform	400 mg.
1-Ethyl-3- [3-ethyl-2 (3H-benzoxazolylidine] oxyindole	80 mg.
Bis (cyclopentadienyl) niobium tribromide	8 mg.
Chlorbenzene	200 ml.
Tetrachlorophthalic anhydride	80 mg.

The exposure amount needed 830 lux.sec. When bis (cyclopentadienyl) niobium tribromide was not contained, the exposure amount was 1540 lux.sec.

Example 19

Poly-9-vinylcarbazole (trade name Luvican M-170 supplied by BASF)	8 g.
Iodoform	400 mg.
Triphenylbismuthine	4 mg.
2, 4, 7-Trinitro-9-fluorenone	50 mg.
Benzene	200 ml.
Diphenyl chloride	2 g.

The exposure amount needed 55 lux.sec. When triphenylbismuthine was not contained, the exposure amount was 170 lux.sec.

Example 20

N,N,N',N'-tetrabenzyl-P-phenylendiamine	4 g.
Polyvinylbutylal resin (trade name S-lec ELS supplied by Sekisui Kagaku)	4 g.
Hexabromodimethylsulfoxide	400 mg.
3-Ethyl-5- [3-ethyl-2(3H)-benzothiazolylidene] rhodanine	60 mg.
Bis (cyclopentadienyl) chromium	4 mg.
Toluene	200 ml.

The exposure amount needed 1,170 lux.sec. When bis (cyclopentadienyl) chromium was not contained, the exposure amount was 1,920 lux.sec.

Example 21

Bis-4,4'-dialkylaminobenzylideneazine	4 g.
Copolymerization resin of acrylonitrile and styrene (trade name Estylene AS-61NT supplied by Yahata Kagaku)	4 g.
Di-tertiallybutylperoxide	400 mg.
4-(4'-dimethylaminophenyl)-5-(4''-chlorphenyl) imidazole	80 mg.
Bis (cyclopentadienyl) tantalum tribromide	16 mg.
Methylene chloride	200 ml.

The exposure amount needed 870 lux.sec. When bis (cyclopentadienyl) tantalum tribromide was not contained, the exposure amount was 1,880 lux.sec.

Example 22

Nitrated poly-9-vinylcarbazole (having 0.06 mole of nitro radical per one carbazole unit mainly at 3-position of carbazole ring)	8 g.
Bromoform	400 mg.
Triphenylbismuthine	16 mg.
Benzene	200 ml.

The exposure amount needed 270 lux.sec. When triphenylbismuthine was not contained, the exposure amount was 530 lux.sec.

Example 23

Leuco crystalviolet	4 g.
Epoxy resin (trade name Epikote 1004 supplied by Shell Oil)	4 g.
2-Azo-bis-isobutylonitrile	400 mg.
4- [4-(P-dimethyl aminophenyl)-1,3-butadienyl] quinoline	80 mg.
Bis (cyclopentadienyl) vanadium	4 mg.
Benzene	200 ml.

The exposure amount needed 2,060 lux.sec. When bis (cyclopentadienyl) vanadium was not contained, the exposure amount was 3,750 lux.sec.

Example 24

Bis-4,4-diallylaminobenzylidene-azine	4 g.
Modified phenolic resin (Beckacite 1100, trade name, supplied by Japan Reichhold Chemical Co.)	4 g.
Tribromomethylphenylsulfone	400 mg.
1,3,5-Triphenylpyrazoline	80 mg.
Tetraphenyl tin	16 mg.
Chlorobenzene	200 ml.

The exposure amount needed 640 lux.sec. When tetraphenyl tin was not contained, the exposure amount was 1,770 lux.sec.

Example 25

Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by BASF)	8 g.
Tribromomethylsulfone	400 mg.
Tetraphenyl lead	16 mg.
Benzene	200 ml.

The exposure amount needed 440 lux.sec. In the absence of tetraphenyl lead the exposure amount was 1,280 lux.sec.

Example 26

Leuco malachite green	4 g.
Polystyrene resin (Piccolastic D-100, trade name, supplied by ESSO)	4 g.
Diphenylthiocarbazone	400 mg.
2-(P-Dimethylaminostyryl) quinoline	150 mg.
Bis (cyclopentadienyl)-P-pentacarbon-monooxide-bimolybdenum	4 mg.
Benzene	100 ml.
Methylene chloride	100 ml.

The exposure amount needed 2,300 lux.sec. In the absence of bis (cyclopentadienyl)-P-pentacarbon-monooxide-bimolybdenum, the exposure amount was 4,150 lux.sec.

Example 27

Leuco malachite green	4 g.
Polycarbonate resin (Panlite C, trade name, supplied by Teijin)	4 g.
2-Azo-bis-isobutyronitrile	400 mg.
2-(4'-Diethylaminophenyl)-4-(4'-dimethylaminophenyl)-5-(2'-chlorophenyl) oxazole	80 mg.
Bis (cyclopentadienyl)-P-hexacarbonmonoxide-bitangsten	4 mg.
Methylene chloride	200 ml.

The exposure amount needed 920 lux.sec. In the absence of bis (cyclopentadienyl)-P-hexacarbonmonooxide-bitungsten, the exposure amount was 1,650 lux.sec.

Example 28

4,4'-Bis-dimethylamino-benzophenone	4 g.
Polycarbonate resin (Iupilon E, trade name, supplied by Mitsubishi Edogawa Kagaku)	4 g.
Carbon tetrabromide	400 mg.
Triphenylbismutin	4 mg.
Methylene chloride	200 ml.

The exposure amount needed 100 lux.sec. In the absence of triphenylbismutin, the exposure amount was 290 lux.sec

Example 29

Leuco crystal violet	4 g.
Acrylonitrile-styrene copolymer (Estylene AS-61NT, trade name, supplied by Yahata Kagaku)	4 g.
2-Azobisisobutyronitrile	400 mg.
3-Ethyl-5- [3-ethyl-2(3H)-benzoxazolylidene] rhodanine	200 mg.
Nickelocene	4 mg.
Methylene chloride	200 ml.

The exposure amount needed 1,590 lux.sec. In the absence of nickelocene, the exposure amount was 4,930 lux.sec.

Example 30

Leuco crystal violet	4 g.
Epoxy resin (Epikote 1004, trade name, supplied by Shell Petroleum Co.)	4 g.
Hexabromodimethylsulfoxide	400 mg.
o - tolydine	100 mg.
Hydrogenated bis (cyclopenta-dienyl) rhenium	2 mg.
Benzene	200 ml.

The exposure amount needed 750 lux.sec. In the absence of hydrogenated bis (cyclopentadienyl) rhenium, the exposure amount was 1,510 lux.sec.

Example 31

Bis-4,4'-diallylamino-benzylidene azine	4 g.
Acrylonitrile-styrene copolymer (Estylene AS-61NT, trade name, supplied Yahata Kagaku)	4 g.
Iodoform	400 mg.
Bis (cyclopentadienyl) iron dicarbonyl	2 mg.
Methylene chloride	200 ml.
Acridine yellow	20 mg.
Chloranil	70 mg.

The exposure amount needed 520 lux.sec. In the absence of bis (cyclopentadienyl) iron dicarbonyl, the exposure amount was 950 lux.sec.

Example 32

Leuco malachite green	4 g.
Polystyrene resin (Piccolastic D-100, trade name, supplied by ESSO)	4 g.
Diphenylthiocarbazone	400 mg.
Vinylcarbazole	50 mg.
Brominated bis (cyclopentadienyl) cobalt	4 mg.
Benzene	100 ml.
Methylene chloride	100 ml.

The exposure amount needed 2,400 lux.sec. In the absence of brominated bis (cyclopentadienyl) cobalt, the exposure amount was 90,400 lux.sec.

Example 33

N,N,N',N'-tetrabenzyl-p-phenylenediamine	4 g.
Modified phenolic resin (Beckacite 1100, trade name, supplied by Japan Reichhold Chemical Co.)	4 g.
Bromoform	400 mg.
Tetraphenyl tin	4 mg.
Benzene	200 ml.

The exposure amount needed 1,550 lux.sec. In the absence of tetraphenyl tin, the exposure amount was 2,250 lux.sec.

Example 34

Bis-4,4-diallylaminobenzylidene azine	4 g.
Modified phenolic resin (Beckacite 1100, trade name, supplied by Japan Reichhold Chemical Co.)	4 g.
Tribromomethylphenylsulfone	400 mg.
Hexaphenylditin	4 mg.
Chlorobenzene	200 ml.

The exposure amount needed 720 lux.sec. In the absence of hexaphenylditin, the exposure amount was 1,120 lux.sec.

Example 35

Leuco malachite green	4 g.
Polystyrene resin (Piccolastic D-100, trade name, supplied by ESSO)	4 g.

Example 35-Continued

Diphenylthiocaroazone	400 mg.
Hexaphenylditin	2 mg.
Benzene	100 ml.
Methylene chloride	100 ml.

The exposure amount needed 2,300 lux.sec. In the absence of hexaphenylditin, the exposure amount was 3,750 lux.sec.

Example 36

Leuco crystal violet	4 g.
Acrylonitrile-styrene copolymer (E stylene AS-61NT, trade name, supplied by Yahata Kagaku)	4 g.
2-Azobisisobutyronitrile	400 mg.
Ferrocene	0.5 mg.
Methylene chloride	200 ml.

The exposure amount needed 600 lux.sec. In the absence of ferrocene, the exposure amount was 2,300 lux.sec.

Example 37

Leuco crystal violet	4 g.
Acrylonitrile-styrene copolymer (Estylene AS-61NT, trade name, supplied by Yahata Kagaku)	4 g.
Diphenylthiocarbazone	200 mg.
Tetraphenylgermanium	8 mg.
2-Azobisisobutyronitrile	200 mg.
Methylene chloride	200 ml.
Orient oil pink OP	20 mg.

The exposure amount needed 780 lux.sec. In the absence of tetraphenylgermanium, the exposure amount was 1,450 lux.sec.

Example 38

Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by BASF)	8 g.
Carbon tetrabromide	400 mg.
Bis (cyclopentadienyl) cerium	8 mg.
Dioxane	200 ml.

The exposure amount needed 100 lux.sec. In the absence of bis (cyclopentadienyl) cerium, the exposure amount was 315 lux.sec.

EXAMPLE 39

Following Example 38, but using bis (cyclopentadienyl) titanium, bis (cyclopentadienyl) chromium, bis (cyclopentadienyl) manganese, or dihalogenated bis (cyclopentadienyl) vanadium in place of bis (cyclopentadienyl) cerium, the exposure amount needed was about 200 lux.sec. for each of them.

Example 40

Iodoform	100 mg.
Triphenylphosphine	4 mg.
Benzene	25 ml.

A solution composed of the above ingredients was placed in a 50 ml. quartz Erlenmeyer flask and irradiated by a high pressure mercury lamp of 100 watt at a distance of 10 cm for about 20 minutes. (When triphenyl phosphine was not contained, the solution was irradiated for 30 minutes.)

Then, a solution obtained by the following ingradients:

poly-3-nitro-9-vinylcarbazole	2 g.
diphenyl chloride	0.5 g.
benzene	25 ml.

was poured into the above-mentioned Erlenmyer flask and mixed with the contents and allowed to stand for three days in a dark place. Then, the solution was coated on an Al laminate paper of 50 μ thick to form a coating of about 5 μ and dried naturally to form a photosensitive paper. The resulting photosensitive paper was given a uniform negative charge of about 350 V by corona charging by using a charging device of about 5.5 KV, contacted with an original positive film, to a 150 watt tungsten lamp at 150 lux.sec. and soaked in a positive liquid developer to form positive images of high fidelity to the original image.

Example 41

Carbon tetrabromide	100.mg.
Vinylcarbazole	50 mg.
Triphenylbismutin	2 mg.
Benzene	25 ml.

A solution composed of the above ingredients was placed in a 50 ml. quartz Erlenmeyer flask, irradiated with a 500 watt xenon lamp at a distance of 10 cm for about 5 minutes. When triphenylbismutin was not used, 30 minute irradiation was necessary.

Then, a solution of 2 g. of poly-9-vinylcarbazole (PO-098, trade name, supplied by Schuchardt) in 25 ml. of benzene was immediately poured into the above-mentioned Erlenmeyer flask and the resulting mixture was allowed to stand in a dark place for 3 days. Then the resulting mixture was coated on an Al plate (0.8 mm thick) to form a coating of about 5 μ thick, and dried naturally to form a photosensitive plate. The resulting photosensitive plate was subjected to an electrophotographic process similar to that of Example 40 and an exposure amount of 110 lux.sec. was required to form positive images of high fidelity to the original image.

Example 42

Pentabromodimethylsulfoxide	100 mg.
Triphenylbismutin	1 mg.
Xylene	25 mg.

A solution composed of the above ingredients was placed in a 50 ml. quartz Erlenmeyer flask, and irradiated by a 500 watt xenon lamp at a distance of 20 cm for about 10 minutes. When triphenylbismutin was not used, 30 minute irradiation was necessary.

Then, a solution of leuco malachite green 1 g. and epoxy resin (Epikote 1004, trade name, supplied by Shell Petroleum Co.) 1 g. in 25 ml. of MEK was immediately added to the Erlenmeyer flask, allowed to stand in a dark place for 2 days, and then 5 ml. of an MEK solution containing 5 mg. of Rose Bengal as a sensitizing dye and 10 mg. of picric acid as Lewis acid was added thereto.

The solution thus obtained was coated on a baryta paper (80 μ thick) which had been treated so as to increase the electroconductivity to form a coating of about 5 μ thick and dried naturally to produce a photosensitive paper. The photosensitive paper thus obtained was subjected to an electrophotographic process similar to Example 40 to produce positive images of high fidelity to the original image. The required exposure amount was 350 lux.sec.

Example 43

(I)	Poly-9-vinylcarbazole	2 g.
	Carbon tetrabromide	50 mg.
	Triphenylbismutin	2 mg.
	Benzene	25 ml.
(II)	Iodoform	50 mg.
	Benzene	25 ml.

A solution of (I) and a solution of (II) were irradiated by a 100 watt high pressure mercury lamp at a distance of about 10 cm for about 5 minutes. (When triphenyl bismutin was not used, the irradiation time was 10 minutes.) Then, these two solutions were immediately mixed, allowed to stand at a dark place for 10 hours, coated on a polyester film (75 μ thick) having an aluminum deposit to form a coating of about 5 μ thick and dried naturally to produce a photosensitive film. The photosensitive film thus obtained was subjected to an electrophotographic process similar to Example 40, and an exposure amount of 120 lux.sec. was required to produce positive images of high fidelity to the original image.

When a solution of poly-9-vinylcarbazole above was used for producing a photosensitive film, an exposure amount of about 58,000 lux.sec. was required to give good positive images.

Example 44

(I)	Poly-3-bromo-9-vinylcarbazole	2 g.
	Bromoform	50 mg.
	Chlorobenzene	25 ml.
(II)	Hexachloroethane	50 mg.
	Triphenylbismutin	2 mg.
	Chlorobenzene	25 ml.

The solutions (I) and (II) were irradiated by a 100 watt high pressure mercury lamp at a distance of about 10 cm for 10 minutes. (When triphenylbismutin was not used, the irradiation time required was 15 minutes.)

Immediately after the irradiation treatment, these two solutions were mixed and allowed to stand in a dark place for about 10 hours. To the resulting mixture was added 10 ml. of a solution of 0.5 g. p-terphenyl in chlorobenzene as plasticizer and coated on an aluminum laminate paper (50 μ thick) to form a coating of about 5 μ thick followed by natural drying to produce a photosensitive paper. The resulting photosensitive paper was given a uniform negative charge of about 350 V by corona charging by using a charging device of 5.5 KV, contacted with an original positive film, exposed to a 150 watt tungsten lamp at 150 lux.sec., and soaked in a positive liquid developer to produce positive images of high fidelity to the original image.

Example 45

(I)	Poly-9-vinylcarbazole (Luvican M-170, trade name, supplied by BASF)	2 g.
	Hexabromodimethylsulfoxide	50 mg.
	Triphenylbismutin	1 mg.
	Benzene	25 ml.
(II)	Pentabromodimethylsulfoxide	50 mg.
	1,6-Dimethoxyphenazine	20 mg.
	Triphenylbismutin	1 mg.
	Benzene	25 ml.

The solutions of (I) and (II) were irradiated by a 500 watt xenon lamp at a distance of about 20 cm for about 5 minutes (When triphenylbismutin was not employed, the required irradiation time was 30 minutes). Immediately after the irradiation treatment, these two solutions were mixed and allowed to stand in a room under a fluorescent lamp for about 24 hours. Then, 5 ml. of a solution of 5 mg. Oil pink in benzene as a sensitizing dye was added thereto, and a photosensitive film was produced in a way similar to Example 44 and subjected to an electrophotographic process similar to Example 44. An exposure amount of 120 lux.sec. was required to produce a positive image of high fidelity to the original image.

Example 46

Poly-9-vinylcarbazole (PO-098, trade name, supplied by Schuchardt)	170 g.
Carbon tetrabromide	10 g.
Triphenylbismutin	340 mg.
Diphenyl chloride	30 g.
Benzene	5 ml.

A solution composed of the above ingredients was coated on a base paper of 60 g/m² (the surface on which the solution is applied was treated with a hydrophilic polymer so as to inhibit the permeation of a solvent) in an amount of about 6 g/m² by a kiss roll coating method and then immediately irradiated by a high pressure mercury lamp (100 watt) at a distance of about 15 cm for 10 seconds. When triphenylbismutin was not used, the required irradiation time was 30 seconds. Then, the coating was dried by hot air at 70°C at a wind velocity of 15 m/sec. to produce a photosensitive paper. The resulting photosensitive paper was subjected to an electrophotographic process similar to Example 44 and the required exposure amount for producing a positive image of high fidelity to the original image was 115 lux.sec.

We claim:

1. An electrophotographic photosensitive member which comprises a support having coated thereon a sensitized layer of photoconductive photosensitive material, said material comprising an organic photoconductive material, a free radical former capable of producing free radicals for sensitizing said organic photoconductive material when uniformly excited by radiation energy and an organometallic compound incapable of liberating free radicals under the exposure used to excite said free radical former, but capable of catalyzing the sensitizing ability of the radical former, said photoconductive photosensitive material having been sensitized by applying said radiation energy uniformly

to at least said free radical former and said organometallic compound.

2. A photosensitive material according to claim **1** in which the organometallic compound is at least one member selected from the group consisting of alkyl metallic compounds, aryl metallic compounds, and alkyl-aryl metallic compounds of a metal element of Group IV B or Group V B of the Periodic Table.

3. A photosensitive material according to claim **2** in which the metal element of Group IV B is a member selected from the group consisting of Ge, Sn and Pb.

4. A photosensitive material according to claim **2** in which the metal element of Group V B is a member selected from the group consisting of P, As, Sb and Bi.

5. A photosensitive material according to claim **2** in which the aryl metallic compound is one of triphenyl metallic compound and tetraphenyl metallic compound.

6. A photosensitive material according to claim **1** in which the organometallic compound is a cyclopentadienyl metallic compound of at least one transition metal element selected from the group consisting of Group III A, IV A, V A, VI A, VII A and VIII A of the Periodic Table.

7. A photosensitive material according to claim **6** in which the transition metal element of Group III A of the Periodic Table is a member selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb.

8. A photosensitive material according to claim **6** in which the transition metal element of Group IV A of the Periodic Table is a member selected from the group consisting of Ti, Zr and Hf.

9. A photosensitive material according to claim **6** in which the transition metal element of Group V A of the Periodic Table is a member selected from the group consisting of V, Nd and Ta.

10. A photosensitive material according to claim **6** in which the transition metal element of Group VI A is a member selected from the group consisting of Cr, Mo, W and U.

11. A photosensitive material according to claim **6** in which the transition metal element of Group VII A is a member selected from the group consisting of Mn, Tc and Re.

12. A photosensitive material according to claim **6** in which the transition metal element of Group VIII A is a member selected from the group consisting of Fe, Co, Ni and Ru.

13. A photosensitive material according to claim **1** in which the content of the organometallic compound is 10^{-3} - 10 percent by weight based on the organic photoconductive material.

14. A photosensitive material according to claim **1** in which the content of the free radical former is 1 – 30 percent by weight based on the organic photoconductive material.

15. A photosensitive material according to claim **1** in which a sensitizing material is incorporated in a mixture of a free radical former and an organic photoconductive material reactively treated by a radiation energy.

16. A photosensitive material according to claim **15** in which the sensitizing material is Lewis acid.

17. A photosensitive material according to claim **15** in which the sensitizing material is a sensitizing dye.

18. A photosensitive material according to claim **15** in which the sensitizing material is a Lewis acid and a sensitizing dye.

19. A photosensitive member according to claim **1** wherein at least one organometallic compound is selected from the group consisting of triphenylbismuthine, triphenylphosphine, tetraphenylarsine, ferrocene and cobaltocene.

20. A photosensitive member according to claim **1** including at least one organic photosensitive material selected from the group consisting of vinyl carbazoles, aromatic amine derivatives, diphenylmethane compounds and triphenylmethane compounds.

21. A photosensitive material according to claim **20** in which the vinyl carbazole is at least one member selected from the group consisting of poly-9-vinylcarbazole, bromine substituted poly-9-vinylcarbazole and iodine substituted poly-9-vinylcarbazole.

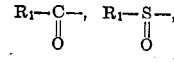
22. A photosensitive material according to claim **20** in which the vinyl carbazole is a member selected from the group consisting of 9-vinylcarbazole copolymer, bromine substituted 9-vinylcarbazole copolymer and iodine substituted 9-vinyl-carbazole copolymer.

23. A photosensitive member according to claim **1** including at least one free radical former selected from the group consisting of polyhalogen containing compound, carbonyl compound, organic sulfur compound, peroxide, azo compound, and diazo compound.

24. A photosensitive material according to claim **23** in which the poly-halogen containing compound is a compound of the formula



where R is selected from the group consisting of hydrogen, alkyl, chlorine, bromine, iodine,



and



where R_1 is selected from the group consisting of substituted or unsubstituted alkyl, aryl and heterocyclic residue; X, Y and Z are, similar or dissimilar, selected from the group consisting of hydrogen, alkyl, Cl, Br and I and at least one of X, Y and Z is halogen atom.

25. A photosensitive material according to claim **24** in which the polyhalogen containing compound is carbon tetrabromide.

26. A photosensitive material according to claim **24** in which the polyhalogen containing compound is bromoform.

27. A photosensitive material according to claim **24** in which the polyhalogen containing compound is iodoform.

28. A photosensitive material according to claim 24 in which the polyhalogen containing compound is a halogenated organic sulfoxide.

29. A photosensitive material according to claim 24 in which the polyhalogen containing compound is a halogenated organic sulfone compound.

30. A photosensitive member according to claim 1 wherein said free radical former is a polyhalogen containing compound and said organic photoconductive material is a vinylcarbazole.

31. A photosensitive member according to claim 1 including a colorization component selected from the group consisting of a dye base or an organic colorization component capable of forming a coloring material by reaction with said free radical former upon radiation excitation.

32. A photosensitive material according to claim 31 in which the dye base compound is selected from the group consisting of leuco bases, carbinol bases, styryl dye bases, cyanine dye bases, merocyanine dye bases and leuco dihydroanthracenes.

33. A photosensitive material according to claim 32 in which the leuco base is a member selected from the group consisting of leuco bases of triphenylmethane dye and leuco bases of diphenylmethane dye.

34. A photosensitive material according to claim 32 in which the carbinol base is selected from the group consisting of carbinol bases of triphenylmethane dye and carbinol bases of diphenylmethane dye.

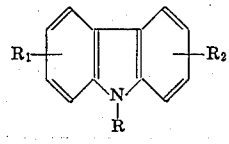
35. A photosensitive material according to claim 31 in which the organic colorization component is a member selected from the group consisting of arylamines, carbazoles, indoles, 1,3,4-oxadiazoles, 1,3,4-triazoles, imidazoles, pyrazolines, aminophenyl substituted oxazoles, benzidines, 1,3-diphenyl-tetrahydroimidazoles, phenazines, acridines, acyl hydrazone derivatives, quinoxalines, N-di-substituted amino containing arylideneazines, pyridines, quinolines, ethylene derivatives, and spiropyran compounds.

36. A photosensitive material according to claim 35 in which the arylamine is a compound of the formula:



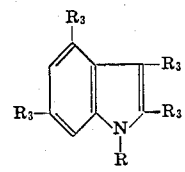
where R is a member selected from the group consisting of hydrogen, alkyl, aryl and aralkyl (substituted or unsubstituted) and R_1 is a member selected from the group consisting of phenyl, α-naphthyl and β-naphthyl and R_2 is a member selected from the group consisting of alkyl, aryl and aralkyl (substituted or unsubstituted).

37. A photosensitive material according to claim 36 in which the carbazole is a compound of the formula:



where R is a member selected from the group consisting of hydrogen, alkyl, alkenyl, aralkyl and aryl (substituted or unsubstituted) and R_1 and R_2 are, similar or dissimilar, selected from the group consisting of hydrogen, alkyl, alkenyl, aralkyl, alkoxy, halogen, and dialkylamino.

38. A photosensitive material according to claim 36 in which the indole is a compound of the formula:



where R is a member selected from the group consisting of hydrogen, alkyl aralkyl and aryl (substituted or unsubstituted) and each R_3 is, similar or dissimilar, selected from the group consisting of hydrogen, alkyl, alkoxy, halogen and dialkylamino.

39. An electrophotographic photosensitive member which comprises a support having coated thereon a sensitized layer of photoconductive photosensitive material, said material comprising an organic photoconductive material, a free radical former capable of producing free radicals for sensitizing said organic photoconductive material when uniformly excited by radiation energy having ultraviolet radiation and an organometallic compound incapable of liberating free radicals under the exposure used to excite said free radical former, but capable of catalyzing the sensitizing ability of the radical former, said photoconductive photosensitive material having been sensitized by applying said radiation energy uniformly having ultraviolet radiation to at least said free radical former and said organometallic compound.

40. The member of claim 29 wherein said photoconductive photosensitive material is sensitized by applying said radiation energy to said organic photoconductive material, said free radical former and said organometallic compound.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,847,607 Dated November 12, 1974

Inventor(s) ICHIRO ENDO ET AL.

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

Title Page, after "Related U.S. Application Data" insert --[30] Foreign Application Priority Data

February 4, 1970 Japan.....45-9836

February 4, 1970 Japan.....45-9838

April 14, 1970 Japan.....45-31850--

Column 4, line 19, "M" should read --m--;

Column 4, line 19, "N" should read --n--;

Column 5, line 39, "IVa" should read --IVA--;

"Va" should read --VA--;

Column 8, line 29, "$\xrightarrow{m}$" should read -- $\xrightarrow{M}$ --;

Column 11, line 5, "E" should read --F--;

Column 23, line 1, "Diphenylthiocaroazone" should read --Diphenylthiocarbazone--;

Claim 40, line 48, "29" should read --39--.

Signed and sealed this 4th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
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C. MARSHALL DANN
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