March 12, 1974 EIICHI KONDO ET AL **3,796,569**

ELECTROPHOTOGRAPHIC PHOTOSENSITIVE MATERIAL

Filed Nov. 11, 1971

FIG. 1

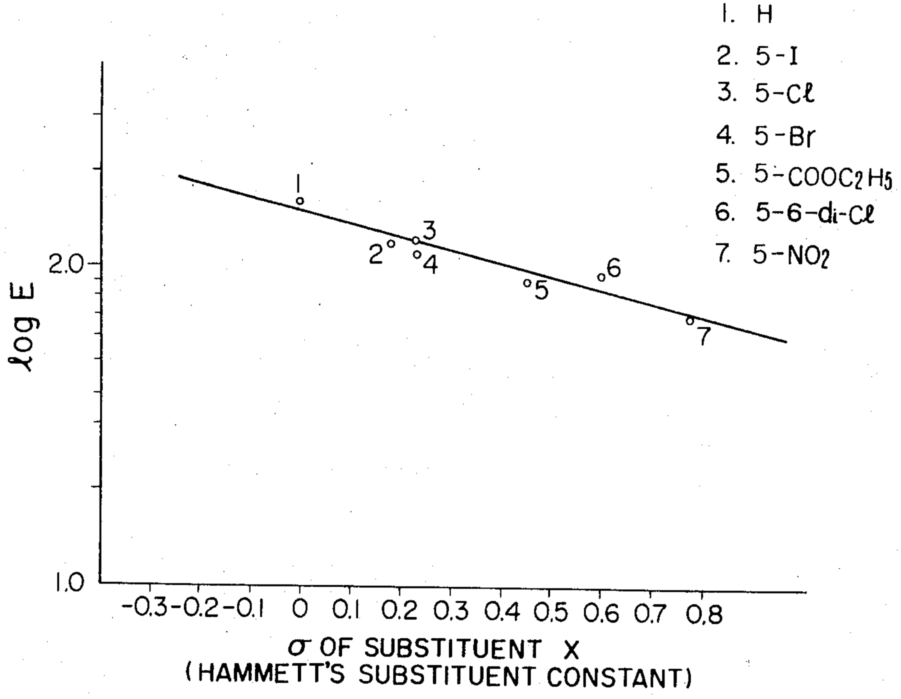


FIG. 2

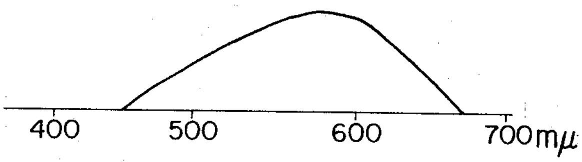


FIG. 3

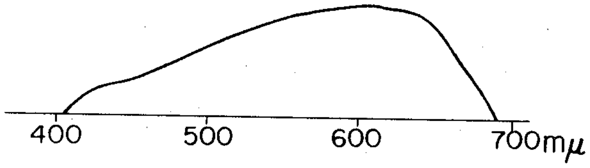
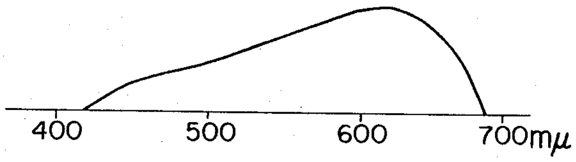


FIG. 4



United States Patent Office

3,796,569
Patented Mar. 12, 1974

3,796,569

ELECTROPHOTOGRAPHIC PHOTOSENSITIVE MATERIAL

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Filed Nov. 11, 1971, Ser. No. 197,754
Claims priority, application Japan, Nov. 17, 1970, 45/101,621
Int. Cl. G03g *5/06*
U.S. Cl. 96—1.6 7 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic photosensitive material which comprises poly-9-vinylcarbazole or derivative thereof and a dialkylaminostyryl dye.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to highly sensitive electrophotographic photosensitive materials mainly composed of organic photoconductive compounds.

Description of the prior art

Among organic photoconductive compounds used as photoelectric photosensitive materials, some have a considerably high sensitivity, but it is very rare that they are used in practice at present. Organic photoconductive compounds have various more excellent characteristics than inorganic ocmpounds and promise various applications in the field of electrophotography. For example, it is possible only by use of organic photoconductive compounds to provide transparent photosensitive films, flexible photosensitive films or photosensitive films which are light in weight and easy to handle. Furthermore, organic photoconductive compounds can give a photosensitive member having film shapeability, surface smoothness and selectivity of charging polarity in an electrophotographic reproduction process. These excellent properties are not expected in the case of an inorganic photoconductive compound. However, organic photoconductive compounds have not been practically used for a photosensitive member of electrophotography in spite of their many excellent properties since their photosensitivity is low.

In the early years the investigation of organic photoconductive compounds was mainly directed to various macromolecule type aromatic or heterocyclic compounds, all of which have a complicated structure, and some highly sensitive organic photoconductive compounds were discovered. However, the recent trend is toward the optical or chemical sensitization in order to attain higher sensitivity because even a known organic photoconductive compound having the highest sensitivity cannot be used without optical or chemical sensitization as its sensitivity is too low to be used in practice. It is, therefore, essential to utilize the most effective optical or chemical sensitization when organic photoconductive compounds are used in practice, and the commercial values of organic photoconductive compounds are dependent upon how they are optically or chemically sensitized to provide photosensitive materials having a sufficiently high sensitivity.

The most general sensitization method is to add sensitizing dyes or Lewis acid, and these two methods can be applied to all of organic photoconductive compounds without exception. When the sensitizing dye is added, their specific spectral absorptions are added to those of the organic photoconductive compounds. When Lewis acid is added, the complex of doner and acceptor is formed between the organic photoconductive compound and the Lewis acid so that the new spectral sensitivity bands (C—T band) appear.

However, the sensitivity attained by the above described methods is still too low to be used in the electrophotographic process.

There have been known various organic photoconductive compounds, and they are, for example,

(A) Vinylcarbazoles: poly-9-vinylcarbazole, 9-vinylcarbazole copolymer, 3-nitro-9-vinylcarbazole copolymer, nitrated poly-9-vinylcarbazole, poly-9-vinyl-3-aminocarbazole, 3 - N - methylamino-9-vinylcarbazole copolymer, halogen-substituted poly-vinylcarbazole, poly-3,6-dibromo-9-vinylcarbazole, 3,6 - dibromo-9-vinylcarbazole copolymer, brominated poly-9-vinylcarbazole, 3-iodo-9-vinylcarbazole copolymer, poly-3,6-diiodo-9-vinylcarbazole, poly-3-benzylideneamino-9-vinylcarbazole, poly-9-propenylcarbazole, graft copolymer of 9-vinylcarbazole and ethylacrylate (90:10 in polymerization mol ratio), vinylanthracene-9-vinylcarbazole copolymer, homopolymer or copolymer of 2-(or 3-) vinyl-9-alkylcarbazole (where alkyl group is a primary alkyl group such as methyl, ethyl, propyl, etc.) and the like.

(B) Aromatic amino derivatives: aminopolyphenyl, arylideneazines, N,N′-dialkyl-N,N′-dibenzylphenylenediamine, N,N,N′,N′-tetrabenzyl-p-phenyldiamine, N,N′-diphenyl-p-phenylenediamine, N,N′-dinaphthyl - p - phenylenediamine, 4,4′ - bis-dimethylaminobenzophenone, and the like.

(C) Diphenylmethane and triphenyl methane series: diphenylmethane dye leuco base, triphenylmethane dye leuco base, and the like.

(D) Heterocyclic compounds: oxadiazole, 9-ethylcarbazole, 9-n-hexylcarbazole, 5-aminothiazole, 1,2,4-triazole, imidazoline, oxazole, imidazole, pyrazoline, imidalizine, polyphenylenethiazole, 1,6-methoxyphenazine, α,ω-bis-(9-carbazole)-alkane derivative, pyrazolinopyrazoline derivatives, and the like.

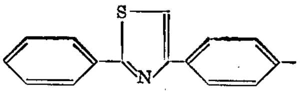
(E) Those having condensed rings: benzthiazole, benzimidazole, 2-(4′-diaminophenyl) benzoxazole, 2-(4′-dimethylaminophenyl) benzoxazole, aminoacridine, quinoxaline, diphenylenehydrazones, pyrrocoline derivatives, 9,10-dihydroanthracene derivatives, and the like.

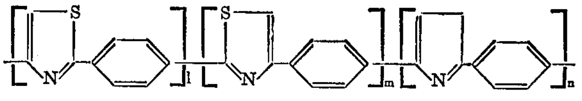
(F) Compounds having a double bond: acylhydrazone, ethylene derivatives, 1,1,6,6-tetraphenylhexatriene, 1,1,5-triphenyl-pent-1-ene-4-ine-3-ol; and the like.

(G) Condensation compounds: condensation compounds of aldehyde and aromatic amines, reaction products of secondary aromatic amines and aromatic halogenides, polypyromethanoimide, poly - P - phenylene-1,3,4-oxadiazole, and so on.

(H) Vinylpolymers (except polyvinylcarbazoles): α-alkylacrylamide polymers; polyvinylacridine, poly-[1,5-diphenyl-3-(4-vinylphenyl)-2-pyrazoline]; poly (1,5-diphenylpyrazoline); polyacenaphthylene; nucleus-substituted-polyacenaphthylene; polyvinylanthracene; poly-2-vinyldibenzothiophene, and so on.

(I) Organic photoconductive oligomers:





where *l*, *m* and *n* are 0 or *l* and $l \geqq m \geqq n$.

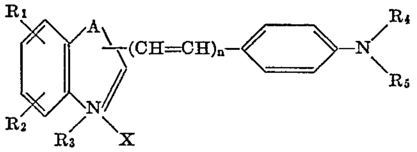
Examples of oligomers are:

as 5 ring compound
p-bis-(2-phenyl-4-thiazolyl)benzene, as 7 ring compound
2,4-bis-[4-(2-phenyl-4-thiazolyl)-phenyl]thiazole and as 9 ring compound
1,4 - bis - [4 - {4 - (2 - phenyl - 4 - thiazole)-phenyl}-thiazolyl]benzene.

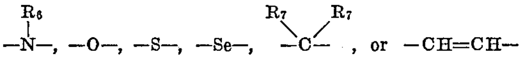
Some of the above listed organic photoconductive compounds may be sensitized by the prior art sensitization methods to have a sufficiently high sensitivity, but the others are not sufficiently sensitized. It is therefore desired to find out a suitable sensitization method depending upon the kinds of organic photoconductive compounds whereby they are satisfactorily utilized as the electrophotographic photosensitive materials.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided an electrophotographic photosensitive material which comprises an organic photoconductive material selected from the group consisting of poly-9-vinylcarbazole and derivatives thereof and at least one of dialkylaminostyryl dyes having the formula:



where A is



$-N(R_6)-$, $-O-$, $-S-$, $-Se-$, $-C(R_7)(R_7)-$, or $-CH=CH-$

wherein R_6 is hydrogen or loweralkyl (including loweralkenyl) and R_7 is, similar or dissimilar, selected from the group consisting of hydrogen and loweralkyl (including loweralkenyl); R_1 and R_2 are, similar or dissimilar, selected from the group consisting of hydrogen and substituents having Hammett's substituent constant σ not lower than 0.2, but R_1 and R_2 should not be simultaneously hydrogen; R_3 is an alkyl having 6 to 12 carbon atoms; R_4 and R_5 are, similar or dissimilar, loweralkyl; X is an anion; and *n* is 1 or 2.

An object of this invention is to provide an excellent method of sensitizing organic photoconductive compounds and further to provide an organic photosensitive material for electrophotography of high photosensitivity which can be practically used.

Another object of this invention is to provide a photosensitive film which is highly sensitive, transparent, flexible, light and of easy handling.

A further object of this invention is to provide a photosensitive material which is sensitive to all visible lights.

Another object of this invention is to provide a photosensitive material for multicolor electrophotography capable of color separation photographing by using a color separation filter.

A further object of this invention is to provide a stable organic photoconductor photosensitive material which potential characteristics such as surface potential, dark decay and the like are not disturbed by the addition of a sensitizing dye.

Another object of this invention is to provide an organic photoconductor photosensitive plate in which the compatibility of an organic photoconductor and a sensitizing dye is so excellent that there is not a fluctuation of quality upon production.

BRIEF DESCRIPTION OF THE DRAWING

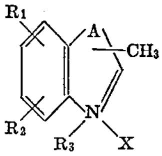
FIG. 1 is a graph showing a relation between log E where E is photosensitivity as defined in Example 1 below and σ value; and

FIG. 2, FIG. 3 and FIG. 4 show spectral sensitivity of some dialkylaminostyryl dyes used in this invention.

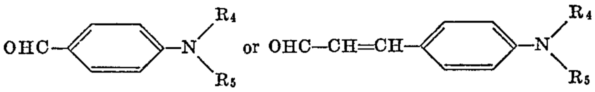
DESCRIPTION OF THE PREFERRED EMBODIMENTS

Dialkylaminostyryl dyes used in the present invention may be prepared by conventional methods, for example, as shown below.

(1) A compound of the formula



is condensed with a compound of the formula



by heating them in an alcohol in the presence of piperidine.

In the above formulas, R_1, R_2, R_3, R_4, R_5, A and X are as defined above.

(2) The reactants are heated in acetic anhydride to condensate them.

The present inventors have found that the above mentioned dialkylaminostyryl dye is particularly effective for poly-9-vinylcarbazole or derivatives thereof as a sensitizer. The range sensitized by the dialkylaminostyryl, dye according to this invention widely covers whole visible wave length, and particularly shows high response to green light. In examples, there are given comparisons between the sensitization according to this invention and that caused by a compound having a chemical structure similar to the dialkylaminostyryl dye within the scope of this invention. The difference of the sensitizing effect therebetween is remarkable and it has been found that there is a certain rule with respect to the substituent effect.

The mechanism of dye sensitization to organic photoconductive compounds is not yet generally known, but the present inventors have recognized that sensitization effect of dye is, in general, closely related to the chemical structure of the dye. The present inventors have found that the larger the electron attractivity of substituent on the benzenoid moiety of the nucleus containing "A" and "N" in the above formula such as imidazole, oxazole, thiazole, selenazole, pyrrole and pyridine rings, the higher the sensitization effect.

When at least one of R_1 and R_2 is a halogen such as Cl, Br and I, nitro or $COOR_8$ where R_8 is loweralkyl, the dialkylaminostyryl dye shows far better sensitization effect than that having unsubstituted benzenoid moiety of the nucleus containing "A" and "N." R_4 and R_5 are preferably lower alkyl of not higher than C_4. The sensitization effect of the substituent is approximately proportional to the Hammett's substituent constant (σ). As illustrated in FIG. 1 where the ordinate is log E where E is photosensitivity and abscissa is Hammett's σ value, the relation is shown by a straight line.

Hammett's substituent constant is described in L. P. Hammett: "Physical Organic Chemistry," page 78 (published by McGraw-Hill Book Co., N.Y., 1940) and D. H. McDaniel, H. C. Brown: J. Org. Chem. 23, 420 (1958).

σ values of representative substituents are shown in Table 1 below.

TABLE 1

Substituent	σ Value	Substituent	σ Value
$P-OCH_3$	−0.268	m-I	+0.352
$m-OCH_3$	+0.115	$P-COOC_2H_5$	+0.450
$P-CH_3$	−0.170	$m-COOC_2H_5$	+0.370
$m-CH_3$	−0.069	P-CN	+0.660
P-Cl	+0.227	m-CN	+0.560
m-Cl	+0.373	$P-CF_3$	+0.540
P-Br	+0.232	$m-CF_3$	+0.430
m-Br	+0.391	$P-NO_2$	+0.778
P-I	+0.180	$m-NO_2$	+0.710

The Hammett's value used in the present invention is higher than 0.2, preferred with from 0.2 to 0.8. A particularly preferable value ranges from 0.35 to 0.8.

Carbon number of alkyl of R_3 in the general formula of dialkylaminostyryl dye used in this invention remarkably affects the sensitization ability of the dialkylaminostyryl dye. This will be shown later.

In case of silver halide photosensitive material, there are measured spectral reflectivity of dialkylaminostyryl dye absorbed to the surface of silver halide, and monomer absorption, dimer absorption and aggregation absorption are known.

In the present invention, a relation among carbon number of R_3 in the general formula of the dialkylaminostyryl dye, spectral reflectivity of dialkylaminostyryl dye in poly-9-vinylcarbazole and sensitization efficiency is investigated and the following matter is observed. When carbon number of R_3 is 2–5, there are observed aggregation absorption, dimer absorption and trimer absorption while at carbon number of R_3 being 6 or more the aggregation absorption is hardly observed, but only monomer absorption and dimer absorption are observed.

Further, it is observed that the sensitization efficiency is inversely proportional to the amount of aggregation absorption and carbon number of 6 or more gives particularly high sensitivity.

A dialkylaminostyryl dye having R_3 of more than 12 carbon atoms cannot be easily synthesized and is obtained at low yield. Therefore, such a dialkylaminostyryl dye is not advantageous from a commercial point of view.

Representative organic photoconductive compounds used in this invention are:

poly-9-vinyl carbazole (cf. U.S. Pat. 3,037,861);
poly-3-vinyl-9-alkyl carbazole (cf. ibid.);
chlorinated poly-9-vinyl carbazole (chlorine content, 2–43% by weight), for example, poly-3-chloro-9-vinylcarbazole, poly-3,6-dichloro-9-vinylcarbazole (Belgian Pat. 753,619);
brominated poly-9-vinylcarbazole (bromine content, 17–46% by weight), for example, poly-3,6-dibromo-9-vinylcarbazole etc. (Japanese Patent Publication Nos. 19,751/1969 and 25,230/1967);
chlorinated brominated poly-9-vinylcarbazole;
chlorinated iodinate poly-9-vinylcarbazole;
cyanated poly-9-vinylcarbazole;
thiocyanated poly-9-vinylcarbazole (the above two compounds are described in Japanese Patent Application Nos. 15,055/1970 and 98,528/1970) poly-3-methyl-9-vinylcarbazole;
and chlorinated poly-3-methyl-9-vinylcarbazole, for example poly-3-methyl-6-chloro-9-vinylcarbazole (Japanese Patent Application No. 66,005/1970).

It is known that the above mentioned polyvinyl carbazole and derivatives thereof have specific stereostructures. This specific configuration causes overlap of π-electron of carbazole ring and thereby a particularly excellent photoconductivity is obtained.

However, poly-9-vinylcarbazole and derivatives thereof are sensitive only to ultraviolet region, but not to visible light. Therefore, photosensitivity of non-sensitized photosensitive plate of poly-9-vinylcarbazole series for tungsten lamp is about 10^4 lux.sec. and is almost the same as that of non-sensitized photosensitive plate composed of a photoconductor of low molecular weight and a binder resin.

However when the poly-9-vinylcarbazoles are sensitized by cyanine dye according to this invention, the photosensitive plate made of them shows photosensitivity of 2×10^1 to 10^2 lux.sec. while the photosensitive plate composed of a photoconductor of low molecular weight and a binder resin sensitized according to this invention shows a photosensitivity of 5×10^2 to 5×10^3 lux.sec. Therefore, the photosensitivity obtained by this invention is about ten times that of the conventional one.

Some preparation methods of poly-9-vinylcarbazole derivatives used in this invention are shown below.

Chlorinated poly-9-vinylcarbazole, brominated poly-9-vinylcarbazole, and chlorinated brominated poly-9-vinylcarbazole may be prepared by reacting poly-9-vinylcarbazole with an appropriate chlorinating agent and/or brominating agent. 9-(β-chloroethyl) carbazole or 9-(β-hydroxyethyl) carbazole is chlorinated or brominated followed by dehydrochlorination and dehydrating treatment to give chlorinated or brominated vinylcarbazole. The resulting vinylcarbazole is homopolymerized or copolymerized to produce the halogenated poly-9-vinylcarbazoles. Chlorinated poly-9-vinylcarbazole is obtained by reacting a chlorination agent such as chlorine or sulfuryl chloride with poly-9-vinylcarbazole. Some examples of syntheses will be described below.

PREPARATION EXAMPLE 1

Four grams of poly-9-vinylcarbazole (trademark "Luvican M–170" from BASF Corp.) is dissolved in 200 ml. of dried methylene chloride in a flask provided with a reflux condenser having a potassium chloride tube and a dropping funnel. Methylene chloride solution (20% by volume) of surfuryl chloride is added at 0° C. with stirring. After adding, the reaction is continued for three hours at the temperature described below. The reaction solution is added to a large quantity of methanol to precipitate polymer, and the precipitated polymer is washed with methanol and dried.

Experiment No.	SO_2Cl_2 added to 20% solution, ml.	Reaction temperature, ° C.	Yield, grams
1	257	0	4.1
2	5.40	20	4.2
3	10.77	20	4.5
4	21.54	30	5.2

Chlorinated poly-9-carbazole is purified by reprecipitation from monochlorobenzene-methanol.

Analysis:

Experiment No.	Cl	N
1	4.25	7.00
2	8.40	6.32
3	15.2	6.30
4	27.8	5.25

The resulting chlorinated poly-9-vinylcarbazole contains chlorine substantially equivalent to that in sulfuryl chloride used. When it is desired to obtain chlorinated poly-9-vinylcarbazole with a high chlorine content (especially higher than 30%), monochlorobenzene solvent is used.

PREPARATION EXAMPLE 2

This is an example of obtaining chlorinated-brominated 9-vinylcarbazole.

4.0 grams of 3-chlorocarbazole is suspended in 20 ml. of carbon bisulfide and while the mixture is refluxed, the solution of 3.2 grams of bromine in 220 ml. of carbon bisulfide is dropped for one hour. After cooling at room temperature, crystals are obtained by filtration and recrystallized from glacial acetic acid. 4.5 grams of 3-chloro-6-bromocarbazole are obtained with a yield of about 80%, melting point 198° C. (197–198° C. in literatures). 3-chloro-6-bromocarbazole may be obtained by brominating carbazole into 3-bromocarbazole (M.P.=201° C.) and then chlorinating it. 4.0 grams of 3-chloro-6-bromocarbazole, 0.07 gram of caustic potash powder and 5 ml. of methylcyclohexane are reacted in an autoclave 100 ml. in volume at 170° C. for six hours while introducing acetylene (the initial gage pressure=about 25 atms.). After cooling, the reaction product is poured into water and the precipitants are obtained by filtration and recrystallized from n-hexane solution. 3.3 grams of

3-chloro-6-bromo-9-vinylcarbazole is obtained with a yield of 76% and melting point 135° C.

Analysis.—Found (percent): C, 54.0; H, 2.86; N, 4.50; Cl, 11.0; Br, 25.0. Calcd. (percent): C, 54.8; H, 2.94; N, 4.57; Cl, 11.6; Br, 26.1.

3-chloro-6-bromo-9-vinylcarbazole may be obtained by brominating 9-β-chloroethylcarbazole or 9-ethylolcarbazole and then chlorinating and treating with alcoholic caustic potash. Next 1.0 gram of 3-chloro-6-bromo-9-vinylcarbazole in 3.0 ml. of acetonitrile in a hard glass polymerization tube is exposed to a high-pressure mercury vapor lamp, and the exposing is continued for thirty minutes after gelation. Then methanol is added and the resulting precipitate is separated by filtration, dissolved into benzene and then precipitated again by adding methanol. These steps are repeated twice. 0.6 gram of white polymer is obtained with a yield of about 60%, and the intrinsic viscosity in benzene is $[\eta]=0.45$.

Thiocyanated poly-9-vinylcarbazole used as an organic photoconductive compound in this invention may be prepared by the reaction of poly-9-vinylcarbazole with a thiacyanogen as described below. The thiocyanated poly-9-vinylcarbazole may be further obtained by other methods such as reaction of poly-9-vinylcarbazole with sodium thiocyanate and bromine.

PREPARATION EXAMPLE 3

Poly-9-vinylcarbazole (5.0 g.) is dissolved in 160 ml. of chlorobenzene, and then a chlorobenzene solution of a thiacyanogen obtained from lead thiocyanate and equivalent amount of bromine (cf. "Organic Reactions," vol. 3, p. 255) is gradually added thereto with agitation at a temperature lower than −10° C. and the reaction is carried out for 3 hours. The reaction temperature is preferably low as far as the reactivity of the reagent is not deteriorated since a side reaction occurs at high temperature to form gel. Then, the reaction mixture is poured into a large amount of methanol to precipitate the polymer, washed with methanol, and dried under vacuum. The polymer thus obtained is further purified by the reprecipitation from chlorobenzene-methanol. According to the above-mentioned method, the following polymers are prepared.

Polymer	Amount of thiacyanogen (grams)	Reaction temperature (° C.)	Yield (grams)
(1)	0.30	−15	5.1
(2)	0.60	−15	5.2
(3)	1.20	−15	5.5
(4)	1.81	−15	5.7
(5)	3.01	−15	6.3

Analysis and solubility of the above-mentioned polymers are shown below.

Polymer	Analysis (percent)		Solubility			
	S	N	THF	Methylene chloride	Benzene	Benzene
(1)	1.50	7.76	O	O	O	O
(2)	2.95	8.09	O	O	O	O
(3)	5.83	9.10	O	O	O	Δ
(4)	8.22	9.81	O	O	O	X
(5)	12.55	11.08	O	O	Δ	X

NOTE: O=soluble; Δ=hardly soluble; X=insoluble.

In infrared spectrophotometry, the absorption wavelengths are 2145 cm.$^{-1}$ (—C≡N), 860 cm.$^{-1}$ and 790 cm.$^{-1}$ (benzene nucleus substituted at 1, 3 and 4 positions), so that it is considered that —SCN groups are substituted at 3 or at 3 and 6 positions of a carbazole ring.

PREPARATION EXAMPLE 4

Cyanated poly-9-vinylcarbazole may be obtained in the following manner:

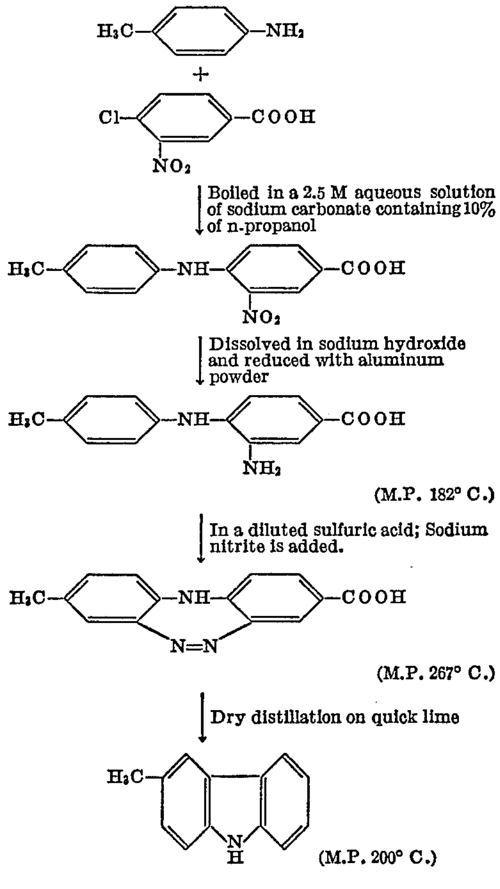
Five grams of poly-9-vinylcarbazole is dissolved into 50 cc. of pyridine and added with 6.6 grams of iodine and is agitated at 110° C. for 3 hours. After being cooled, the mixture is poured into a large quantity of methanol to precipitate the polymer, which is filtered, dried, precipitated again and purified in pyridine-methanol solution. The polymer thus obtained is iodinated-poly-9-vinylcarbazole with an iodine content of 20.49%.

Two grams of iodinated-poly-9-vinylcarbazole is dissolved into 50 cc. of N-methyl-2-pyrrolidone and is added with 0.5 gram of cuprous cyanide. The mixture is agitated at 150° C. for 6 hours. After cooling, the reaction mixture is poured into a large amount of a mixture of methanol and aqueous ammonia (4:1, volume ratio) to precipitate the polymer. The polymer thus precipitated is filtered, dried, reprecipitated with tetrahydrofuran-methanol, and purified. The resulting polymer is white and soluble in organic solvents such as tetrahydrofuran, pyridine, chlorobenzene, and so on. In infrared spectrophotography, the absorption due to the presence of cyano group is observed at 2210 cm.$^{-1}$ while the absorption due to the substitution at 3 position of a carbazole ring was observed at 890 cm.$^{-1}$ and 805 cm.$^{-1}$. No iodine is detected and a nitrogen content 9.65% well corresponds to the calculated value. Therefore it is seen that the above reaction is quantitative and that a cyano group occupies the 3 position of a carbazole ring. Thus the polymer obtained is cyanated poly-9-vinylcarbazole.

Further, examples of preparing poly-3-methyl-9-vinylcarbazole and chlorinated poly-3-methyl-9-vinylcarbazole are shown below.

PREPARATION EXAMPLE 5

3-methylcarbazole is prepared according to the method as described in F. Ullmann: Liebigs Annalen der Chemie, 332 82–104 (1904).



Boiled in a 2.5 M aqueous solution of sodium carbonate containing 10% of n-propanol

Dissolved in sodium hydroxide and reduced with aluminum powder

(M.P. 182° C.)

In a diluted sulfuric acid; Sodium nitrite is added.

(M.P. 267° C.)

Dry distillation on quick lime

(M.P. 200° C.)

The resulting 3-methylcarbazole is heated in acetone together with 1.5 mole of powdered potassium hydroxide and 1.1 mole of β-chloroethyl-p-toluene sulfonate for 5 hours, then poured into water, neutralized to precipitate oily matter. The oily matter thus precipitated crystallizes upon standing. The resulting crystals are recrystallized from methanol to obtain 9-β-chloroethyl-3-methylcarbazole, which is heated with an alcoholic potassium hydroxide to produce 3-methyl-9-vinylcarbazole. The resulting 3-methyl-9-vinylcarbazole is distilled and recrystallized. The 3-methyl-9-vinylcarbazole thus purified (4.0 g.) is placed in a polymerization tube of Pyrex, evacuated with nitrogen, and irradiated by a high pressure mercury lamp at 80° C. to effect the polymerization. After about 6 hours, the polymerization product is dissolved in benzene and then precipitated with methanol to obtain white polymer, poly-3-methyl-9-vinylcarbazole, about 2.8 g. (conversion, 70%, intrinsic viscosity in benzene $[\eta]=0.1$.

PREPARATION EXAMPLE 6

Poly-3-methyl-9-vinylcarbazole (4.0 g.) obtained in Preparation Example 5 is dissolved in 160 cc. of dry chlorobenzene with agitation at 0° C., and 26 cc. of a 20% solution of sulfuryl chloride in methylene chloride is dropwise added thereto, and the reaction is carried out at 30° C. for 4 hours. The reaction mixture is then poured into a large amount of methanol to precipitate the polymer, washed with methanol and dried under vacuum to give a chlorinated poly-3-methyl-9-vinylcarbazole containing about 14% by weight of chlorine.

Chlorinated polyvinylcarbazole used in the present invention as an organic photoconductive compound is described in Japanese patent application Nos. 56,806/1969, 9,837/1970 and 53,816/1970.

Representative dialkylaminostyryl dyes used in the present invention are:

2-p-dimethylaminobenzylidenemethyl-5-iodobenzimidazole-n-hexyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-3-methyl-5,6-dichlorobenzimidazole-n-octyliodide,
2-p-dimethylaminobenzylidenemethyl-3-n-octyl-6-bromobenzimidazole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-3-methyl-5-nitrobenzimidazole-n-heptyl iodide,
2-p-dimethylaminobenzylidenemethyl-3-allyl-5-chlorobenzimidazole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-bromobenzoxazole-n-octyl perchlorate,
2-p-di-i-propylaminobenzylidenemethyl-5,6-dichlorobenzoxazole-n-hexyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-nitrobenzthiazole-n-octyl perchlorate,
2-p-diethylaminobenzylidenemethyl-6-chlorobenzthiazole-n-dodecyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-bromobenzthiazole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-iodobenzthiazole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-dichlorobenzthiazole-n-hexyl iodide,
2-p-dimethylaminobenzylidenemethyl-5-nitrobenzthiazole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-5-carbethoxybenzthiazole-n-nonyl iodide,
2-p-dimethylaminobenzylidenemethyl-6-bromobenzselenazole-n-hexyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-chlorobenzselenazole-n-octyl iodide,
2-p-dimethylaminobenzylidenemethyl-3,3-dimethyl-5-nitroindole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-3,3-dimethyl-5-iodoindole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-3,3-dimethyl-5-bromoindole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-5-bromoindole-n-hexyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-3,3-dimethyl-5-chloroindole-n-octyl perchlorate,
2-p-dimethylaminobenzylidenemethyl-6-nitroquinoline-n-octyl perchlorate,
2-p-di-n-butylaminobenzylidenemethyl-6-iodoquinoline-n-hexyl iodide,
4-p-dimethylaminobenzylidenemethyl-6-nitroquinoline-n-hexyl iodide,
4-p-dimethylaminobenzylidenemethyl-6-bromoquinoline-n-octyl iodide,
2-p-dimethylaminocinnamylidenemethyl-6-iodoquinoline-n-octyl perchlorate,
2-p-dimethylaminocinnamylidenemethyl-6-bromoquinoline-n-hexyl iodide,
2-p-dimethylaminocinnamylidenemethyl-3,3-dimethyl-5-nitroindole-n-hexyl perchlorate, and
2-p-dimethylaminocinnamylidenemethyl-3,3-dimethyl-5-chloroindole-n-octyl perchlorate.

The anion function of the above compounds may be exchanged with anions of other acids to form various compounds.

From an economical point of view, dialkylaminostyryl dyes of the above formula where R_1 and R_2 are selected from chloro, bromo, iodo and nitro and are preferable since synthesis of them is easier than that of other dialkylaminostyryl dyes.

The carbon number of alkyl group of R_4 and R_5 does not largely affect the sensitization ability of the dialkylaminostyryl dye, but solubility thereof in solvents. In general, the more the carbon number, the higher the solubility in solvents.

The electrophotographic photosensitive material according to the present invention may be made into a photosensitive member by dissolving or dispersing the organic photoconductive material, the dialkylaminostyryl dye and if desired, binder, plasticizer or other additives in a solvent, coating on a conductive support and drying, or melting the above-mentioned ingredients and coating on a conductive support, or producing a self-supporting photosensitive film from a solution containing the above-mentioned ingredients by evaporating the solvent or by melting and extruding the above-mentioned ingredients.

The above-mentioned photosensitive material may contain, in addition to dialkylaminostyryl dye, conventional sensitizing dyes as described in, for example, Yuki Gosei Kagaku Kyokai-shi, 24, 1010–1027 (1966), such as crystal violet, malachite green, methylene blue, and the like, and further may contain chemical sensitizers, for example, Lewis acid such as picric acid, 5-nitroacenaphthene, 2,4,7-trinitrofluoroenone, maleic anhydride, chloroacetic acid, and anthraquinone.

The above sensitizing dyes are added to the organic photoconductive material preferably in an amount of 0.01–2% by weight based on the organic photoconductive material. They may be added to a solution of the organic photoconductive material in a form of methanol, chloroform or dimethylformamide solution.

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

EXAMPLE 1

One gram of chlorinated poly-9-vinylcarbazole (chlorine content, 27.5%) was dissolved in 15 ml. of monochlorobenzene. A solution of dialkylaminostyryl dye in chloroform was added to the solution obtained above in an amount of 0.1 mole percent. The resulting solution was coated on a high grade paper processed with polyvinylalcohol by using a wire-bar and dried to produce a photosensitive paper having a photosensitive layer of about 6 microns thick.

The photosensitive paper thus obtained was seasoned and then charged with an electrostatic paper analyzer (supplied by Kawaguchi Denki) and exposed to measure the exposure amount necessary for decreasing the initial potential to 1/10 of the initial potential. The result is shown in Table 2 below as "photosensitivity."

The above-mentioned photosensitive paper was charged and the spectral sensitivity was measured by a spectral camera. The peak is listed in Table 2 below as "photosensitivity peak."

Dialkylaminostyryl dyes used in the present example are represented by the following formula:

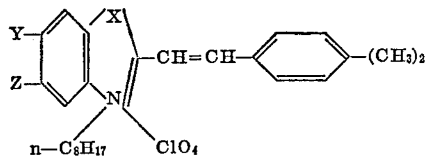


TABLE 2

Dye No.	X	Y	Z	$\lambda_{\max.}$[1]	Photosensitivity [2]	Photosensitivity peak [3]
1	—S—	H	H	526	160	570
2	—S—	I	H	541	120	580
3	—S—	Cl	H	535	120	580
4	—S—	Br	H	540	101	590
5	—S—	$COOC_2H_5$	H	545	90	600
6	—S—	Cl	Cl	552	95	600
7	—S—	NO_2	H	567	70	620
8	$—C(CH_3)_2—$	H	H	548	130	580
9	$—C(CH_3)_2—$	Cl	H	555	95	595
10	$—C(CH_3)_2—$	I	H	556	95	595
11	$—C(CH_3)_2—$	Br	H	563	90	600
12	$—C(CH_3)_2—$	NO_2	H	582	75	620
13	—CH=CH—	H	H	528	120	590
14	—CH=CH—	Cl	H	535	90	605
15	—CH=CH—	I	H	538	90	605
16	—CH=CH—	Br	H	543	80	610
17	—CH=CH—	NO_2	H	569	55	635

[1] Spectral absorption maximum (mμ) in a methanol solution.

[2] Exposure amount (lux.sec.) necessary for decreasing an initial potential to 1/10.

[3] Maximum (mμ) of spectral sensitivity.

In Table 2 above, dye numbers 1, 8 and 13 are not within the scope of the present invention and are given for comparison with dialkylaminostyryl dyes of the present invention. The result shown in Table 2 indicates that when the substituents Y and Z are those having high electron attractivity, the sensitization effect is large.

Spectral sensitivity curves for dye numbers 2, 7, and 12 are shown in FIGS. 2, 3 and 4, respectively.

Reference numbers 1–7 in FIG. 1 correspond to dye numbers 1–7 in Table 2, respectively.

EXAMPLE 2

Two grams of poly-9-vinylcarbazole (Luvican M–170, trade name, supplied by Badische Anilin und Soda-Fabrik) was dissolved in 15 ml. of tetrahydrofuran. 5 mg. of 2-p-dimethylaminocinnamylidenemethyl-6-nitrobenzthiazole-n-octyl perchlorate dissolved in 2 ml. of dimethylformamide was added to the solution obtained above, and then 0.5 g. of chlorinated paraffin (chlorine content, 40%) was added thereto. The resulting solution was coated on an art paper to form a photosensitive layer of 6μ (when dried) thick and dried at 100° C. for 5 minutes. The resulting photosensitive paper was charged, exposed by a photographic enlarger and developed. The optimum exposure was 75 lux.sec. and the spectral photosensitivity peak was 680 mμ.

EXAMPLE 3

Brominated poly-9-vinylcarbazole (bromine content, 14.5%) ____g__	2
Monochlorobenzene ____ml__	20
Dialkylaminostyryl dye (each dye "a" to "e" listed below) ____g__	0.01

The above-mentioned ingredients were mixed uniformly to form a solution. The resulting solution was coated on a polyethyleneterephthalate film having an aluminium vapor deposit layer (transmission rate, 50%) to form a photosensitive layer of 8μ thick. The resulting photosensitive member was charged, imagewise-exposed and developed in a way similar to Example 2 to obtain good images.

The optimum exposure amount for each dye "a" to "e" is shown below.

	Lux.sec.
(a) 2-p-dimethylaminobenzylidenemethyl-3-ethyl-5-bromobenzimidazole-n-octyl perchlorate	360
(b) 2-p-dimethylaminobenzylidenemethyl-6-bromobenzoxazole-n-octyl perchlorate	150
(c) 2-p-dimethylaminobenzylidenemethyl-6-bromobenzselenazole-n-hexyl perchlorate	100
(d) 2-p-dimethylaminobenzylidenemethyl-5-nitroindole-n-octyl perchlorate	70
(e) 2-p-dimethylaminocinnamylidenemethyl-6-bromobenzthiazole-n-dodecyl perchlorate	75

EXAMPLE 4

Poly-9-vinylcarbazole ____g__	2
Carbon tetrabromide ____g__	0.1
9-vinylcarbazole ____g__	0.1
Benzene ____ml__	40

The above ingredients are uniformly mixed and exposed to a 450 w. mercury lamp at a distance of 10 cm. for 5 minutes. After completion of the reaction, 10 mg. of 4-p-dimethylaminobenzylidenemethyl-6-nitroquinoline-n-octyl perchlorate in 5 ml. of chloroform was added to the reaction solution. The resulting solution was coated on a high grade paper having a polyvinylalcohol layer to form a coating of 5μ thick (when dried) followed by drying.

The resulting photosensitive paper was subjected to an electrophotographic process in a way similar to Example 2 and good images were obtained. The optimum exposure amount was 90 lux.sec. while optimum exposure amount for a photosensitive paper containing no sensitizing dye was 150 lux.sec.

EXAMPLE 5

Poly-9-vinylcarbazole [as shown in Table 3, (1) to (5)] ____g__	2.0
0.2% solution of 2-p-dimethylaminobenzylidenemethyl-6-nitrobenzthiazole-n-hexyl perchlorate in chloroform ____ml__	5
Tetrahydrofuran ____ml__	30

The above ingredients were mixed uniformly to form a solution and coated on a high grade paper treated with polyvinylalcohol to form a coating of about 5μ thick. The resulting photosensitive paper was charged, exposed to a light image through a positive original of a photographic dry plate from a xenon lamp by using a photographic enlarger and developed. The sensitivity was shown in Table 3.

TABLE 3

Poly-9-vinylcarbazole type organic photoconductor:	Sensitivity (lux.sec.)
(1) Chlorinated poly-9-vinylcarbazole (chlorine content, 24.8%)	95
(2) Poly-3-bromo-6-chloro-9-vinylcarbazole	95
(3) Chlorinated brominated poly-9-vinylcarbazole (chlorine content, 13.2%; bromine content, 15.0%)	80
(4) Cyanogenated poly-9-vinylcarbazole (nitrogen content, 9.65%)	75
(5) Thiocyanated poly-9-vinylcarbazole (sulfur content, 7.18%)	80

EXAMPLE 6

Organic photoconductor (A to E in Table 4)	g	2.0
Polycarbonate	g	0.5
Methylene chloride	ml	30
2 - p - dimethylaminocinnamylidenemethyl-3,3-dimethyl-5-chloroindole-n-octyl perchlorate	g	0.01

The above ingredients were uniformly mixed to form a solution and applied to a paper treated with polyvinylalcohol to form a coating of 7μ thick (when dried) and dried.

Photosensitive papers not containing any sensitizing dye were also prepared for comparison.

After seasoned, the photosensitive papers were charged with an electrostatic paper analyzer (supplied by Kawaguchi Denki) and exposed to a tungsten lamp and the exposure amount requiring decreasing the potential to ½ of the value of the initial potential was measured. Ratios of reciprocals of the exposure amount are listed in Table 4 below where the reciprocals for C, D and E of non-sensitized photosensitive paper are used as unit.

(A) Poly-9-vinylcarbazole
(B) Chlorinated poly-9-vinylcarbazole (chlorine content, 10.5%)
(C) 4,4'-di-(dimethylamino)-benzophenone
(D) Bis-(4,4'-diallylaminobenzylidene)azine
(E) N,N'-dibenzyl-N,N'-diallyl-m-phenylenediamine

"A" and "B" are organic photoconductive materials within the scope of the present invention while "C" to "E" are controls.

TABLE 4

Organic photoconductive material	Non-sensitized photosensitive paper	Sensitized photosensitive paper
A	2	350
B	2.5	400
C	1	80
D	1	55
E	1	60

EXAMPLE 7

Poly-9-vinylcarbazole (Luvican M–170) (1 g.) was dissolved in 15 ml. of monochlorobenzene, and 0.5 g. of chlorinated paraffin (Empara–40, trade name) was added thereto. In the resulting solution, 2 mg. of dye as shown below per 1 ml. of dimethylsulfoxide was dissolved and coated on a high grade paper having a polyvinylalcohol coating by using a wire-round rod to form a film layer of 5μ thick (when dried) and then dried.

The resulting photosensitive paper was allowed to stand in a constant moistening box of R.H. 60% for two days, and then charged with an electrostatic paper analyzer (supplied by Kawaguchi Denki) and exposed. The exposure amount necessary for decreasing the initial potential to ½ of the original value was measured. The result is shown in Table 5 below.

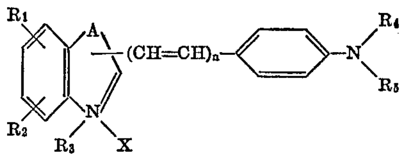
The dyes used in this example have the following formula:

TABLE 5

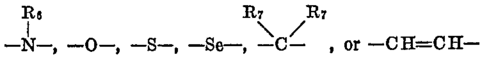
R	Photosensitivity (lux. sec.)	Solubility
C_2H_5	190	Crystal appears somewhat.
n-C_4H_9	125	Do.
n-C_6H_{13}	50	Good.
n-C_8H_{17}	58	Do.
n-$C_{12}H_{25}$	55	Do.

We claim:

1. An electrophotographic photosensitive material which comprises an organic photoconductive material selected from the group consisting of poly-9-vinylcarbazole and derivatives thereof and at least one of dialkylaminostyryl dyes having the formula:



where A is



$$-\overset{R_6}{\overset{|}{N}}-,\ -O-,\ -S-,\ -Se-,\ -\overset{R_7\ \ R_7}{C}-,\ \text{or}\ -CH=CH-$$

wherein R_6 is hydrogen loweralkyl or loweralkenyl and R_7 is, similar or dissimilar, selected from the group consisting of hydrogen and loweralkyl or loweralkenyl; R_1 and R_2 are, similar or dissimilar, selected from the group consisting of hydrogen and substituents having Hammett's substituent constant σ not lower than 0.2, but R_1 and R_2 should not be simultaneously hydrogen; R_3 is an alkyl having 6 to 12 carbon atoms; R_4 and R_5 are, similar or dissimilar, loweralkyl; X is an anion; and *n* is 1 or 2.

2. An electrophotographic photosensitive material according to claim 1 in which the poly-9-vinylcarbazole derivative is selected from the group consisting of chlorinated poly-9-vinylcarbazole (chlorine content, 2–43% by weight), brominated poly-9-vinylcarbazole (bromine content, 17–46% by weight), chlorinated and brominated poly-9-vinylcarbazole, chlorinated and iodinated poly-9-vinylcarbazole, cyanogenated poly-9-vinylcarbazole, thiocyanated poly-9-vinylcarbazole, poly-3-methyl-9-vinylcarbazole, and chlorinated poly-3-methyl-9-vinylcarbazole.

3. An electrophotographic photosensitive material according to claim 1 wherein R_3 is a member selected from the group consisting of n-hexyl, sec-hexyl, n-heptyl, n-octyl, n-dodecyl, n-nonyl and 2-ethylhexyl.

4. An electrophotographic photosensitive material according to claim 1 wherein R_1 is nitro and R_2 is hydrogen.

5. An electrophotographic photosensitive material according to claim 1 wherein R_1 and R_2 are halogens, respectively.

6. An electrophotographic photosensitive material according to claim 1, wherein R_1 is nitro and R_2 is a halogen.

7. An electrophotographic photosensitive material according to claim 1 wherein R_1 is a halogen and R_2 is hydrogen.

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ROLAND E. MARTIN, JR., Primary Examiner

U.S. Cl. X.R.

260—240 D, 240.9