

March 27, 1973

KIKUO KINJO ET AL

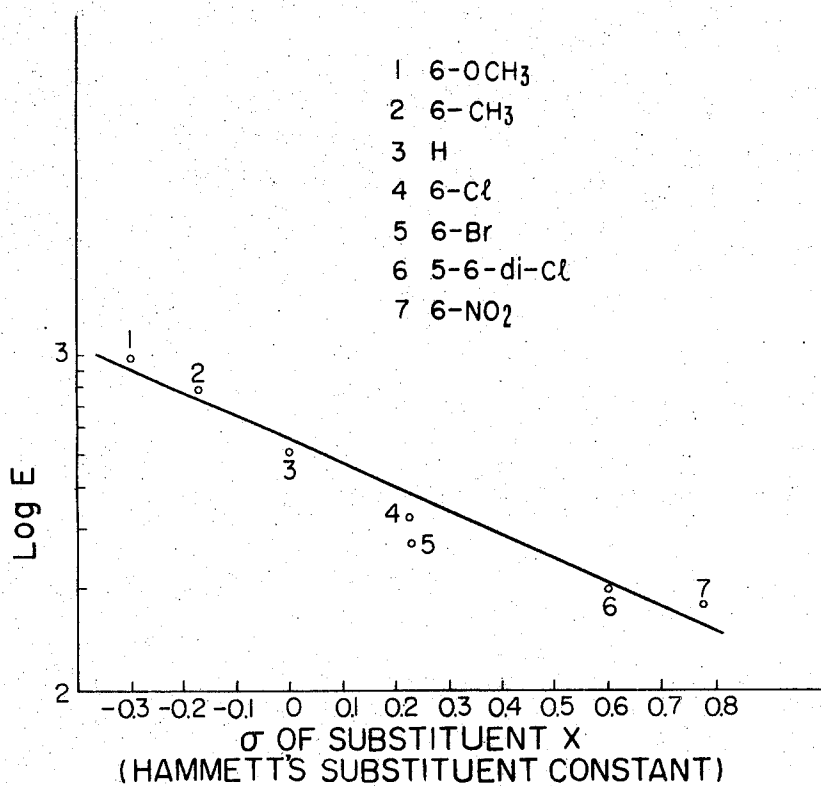
3,723,116

ELECTROPHOTOGRAPHIC PHOTOSENSITIVE MATERIALS

Filed July 20, 1971

3 Sheets-Sheet 1

FIG. 1



March 27, 1973

KIKUO KINJO ET AL

3,723,116

ELECTROPHOTOGRAPHIC PHOTSENSITIVE MATERIALS

Filed July 20, 1971

3 Sheets-Sheet 2

FIG. 2

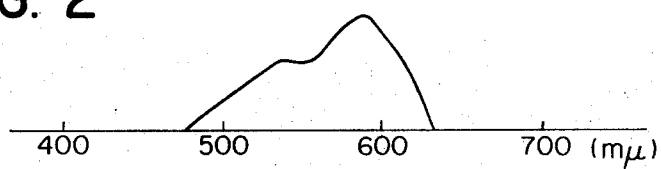


FIG. 3

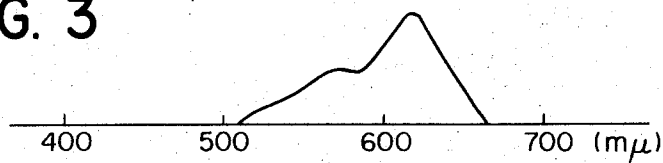


FIG. 4

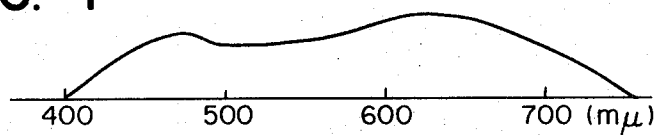
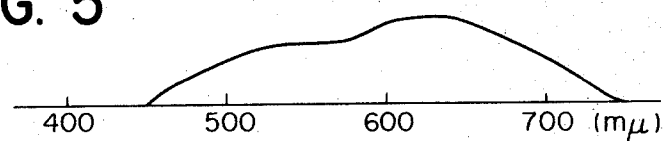


FIG. 5



March 27, 1973

KIKUO KINJO ET AL

3,723,116

ELECTROPHOTOGRAPHIC PHOTSENSITIVE MATERIALS

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3 Sheets-Sheet 3

FIG. 6

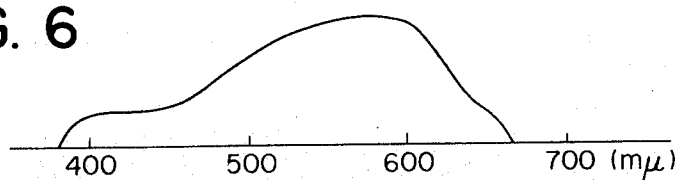


FIG. 7

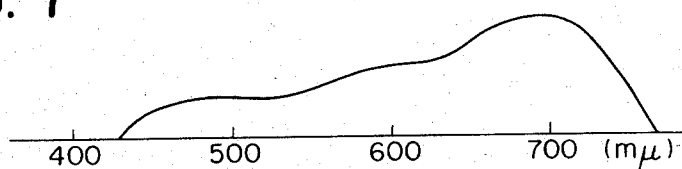
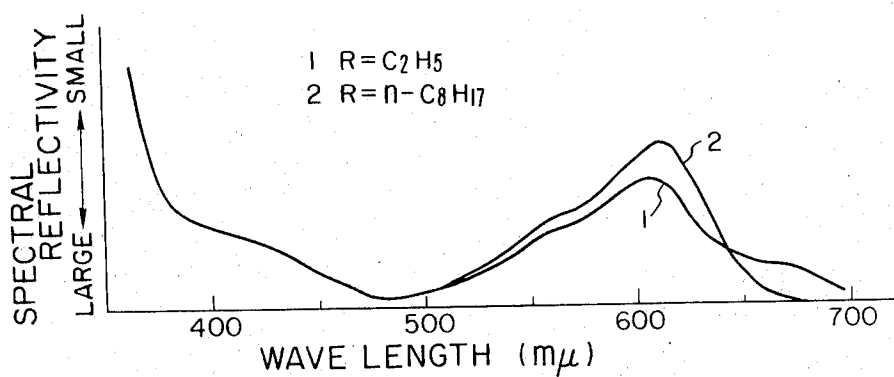


FIG. 8



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ELECTROPHOTOGRAPHIC PHOTOSENSITIVE MATERIALS

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Filed July 20, 1971, Ser. No. 164,340

Claims priority, application Japan, July 24, 1970,

45/64,834; Sept. 25, 1970, 45/84,522

Int. Cl. G03g 5/04

U.S. Cl. 96—1.6

6 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive material comprises a poly-9-vinylcarbazole or its derivative and a cyanine dye. The cyanine dye sensitizes the photosensitivity of poly-9-vinylcarbazole or its derivative and thereby the photosensitive material is suitable for electrophotography.

DETAILED DESCRIPTION OF THE INVENTION

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

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 compounds 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 case of 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 were mainly directed to various macromolecule type aromatic or heterocyclic compounds, all of which have a complicated structure, and some highly sensitive organic photoconductive compounds have been found out. 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 can not 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 donor and acceptor is formed

2

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, imidazoline, 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, pyrocoline 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 1 and $l \geq m \geq n$.

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.

In view of the above demand, the present inventors have studied various organic photoconductive compounds and sensitizers, and formed an excellent combination of an organic photoconductive compound and a sensitizer.

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.

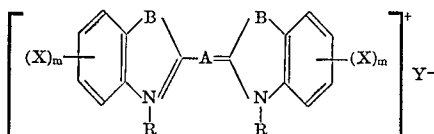
A further object of this invention is to provide a panchromatic photosensitive plate which is sensitive to all visible lights and a photosensitive plate for multicolor electrophotography capable of color separation photographing by using a color separation filter.

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

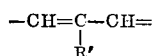
A further object of this invention is to provide an organic photoconductor photosensitive plate of high shelf life.

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.

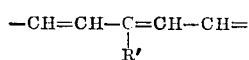
According to this invention, there is provided a photosensitive material which comprises a poly-9-vinylcarbazole or its derivative and a cyanine dye of the formula:



where A is a member selected from the group consisting of $(\text{CH}=\text{CH})_n-\text{CH}=\text{CH}-$ wherein n is an integer of 0 to 2,



and



wherein R' is lower alkyl of C_1 to C_4 ; B is $-\text{S}-$ or $>\text{C}(\text{CH}_3)_2$; R is alkyl of C_6 to C_{12} ; X is, similar or dissimilar, a substituent having Hammett's substituent constant σ of higher than 0.2; m is 1 or 2; and Y is an anion.

The present inventors have found that the above mentioned cyanine dye is particularly effective for the poly-9-vinylcarbazole or derivatives thereof as a sensitizer. The range sensitized by the cyanine dye according to this invention widely covers whole visible wave length, and further the cyanine dye shows high response to blue light, green light and red light when A in the above formula is monomethine, trimethine and pentamethine, respectively.

The sensitizing effect caused by the cyanine dye according to this invention is similar to conventional sensitization by a sensitizing dye in some points, but according to the present invention, the light decay is several to ten times that of conventional sensitizing dyes or conventional cyanine dyes. This will be illustrated in examples appearing later.

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 cyanine 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.

Mechanism of dye sensitization to organic photoconductive compound 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 sensitization efficiency depends upon the electron attractivity of substituent in the general formula of the cyanine dye used in this invention. When the electron attractive group is halogen or nitro, a particularly effective sensitization effect is obtained.

The sensitization effect of the substituent is approximately proportional to the Hammett's substituent constant (σ). As illustrated in FIG. 1 where ordinate is log E 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 below:

Substituent:	σ Value
p- OCH_3	-0.268
m- OCH_3	+0.115
p- CH_3	-0.170
m- CH_3	-0.069
p-Cl	+0.227
m-Cl	+0.373
p-Br	+0.232
m-Br	+0.371
p-I	+0.18
m-I	+0.352
p- COOC_2H_5	+0.45
m- COOCH_3	+0.37
p-CN	+0.660
m-CN	+0.56
p- CF_3	+0.54
m- CF_3	+0.43
p- NO_2	+0.778
m- NO_2	+0.710

5

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

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

In case of silver halide photosensitive material, there are measured spectral reflectivity of cyanine 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 in the general formula of the cyanine dye, spectral reflectivity of cyanine dye in poly-9-vinylcarbazole and sensitization efficiency is investigated and the following matter is observed. When carbon number of R is 2-5, there are observed aggregation absorption, dimer absorption and trimer absorption while at carbon number of R being 6 or more the aggregation absorption is hardly observed, but only monomer absorption and dimer 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.

Cyanine dye having R of more than 12 carbon atoms can not be easily synthesized and is obtained at low yield. Therefore, such cyanine dye is not advantageous from commercial point of view.

Representative organic photoconductive compounds used in this invention are:

poly-9-vinyl carbazole (cf. U.S. Patent 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 iodinated 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 stereostructure. 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 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.

6

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 sulfur chloride with poly-9-vinylcarbazole. Some examples of syntheses will be described below.

Preparation Example 1

Four grams of poly-9-vinylcarbazole (trademark "Luvin 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 sulfur 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 number	SO ₂ Cl ₂ added to 20% solution, ml.	Reaction temperature, ° C.	Yield, gr.
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-vinylcarbazole is purified by reprecipitating from monochlorobenzene-methanol.

Analysis;

Experiment number	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 sulfur 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 cooled at room temperature, crystals are obtained by filtration and recrystallized from glacial acetic acid. 4.5 grams of 3-chloro-6-bromocarbazole is 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.

7

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. 0.60 grams of white polymer is obtained with a yield of about 60%, and the intrinsic viscosity in benzene $[\eta]=0.45$.

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 thiocyanogen 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 thiocyanogen 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 thiocyanogen (g.)	Reaction temperature ($^{\circ}\text{C}$.)	Yield (g.)
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	Chlorobenzene	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 $2,145\text{ cm}^{-1}$ ($-\text{C}\equiv\text{N}$), 860 cm^{-1} and 790 cm^{-1} (benzene nucleus substituted at 1, 3 and 4 positions), so that it is considered that $-\text{SCN}$ 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.

8

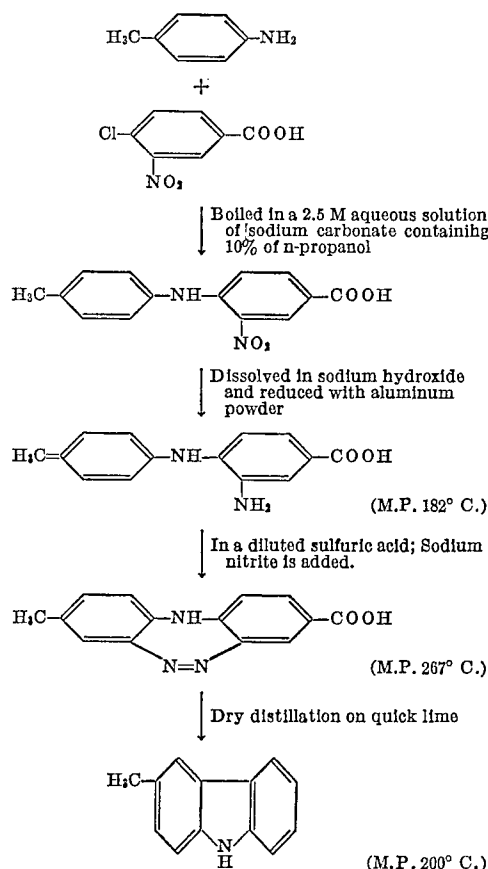
The polymer thus obtained is iodinated-poly-9-vinylcarbazole with an iodine content of 20.49%.

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 cooled, 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 of quantitative and that a cyano group occupies at 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).



The resulting 3-methylcarbazole is heated in acetone together with 1.5 moles of powdered potassium hydroxide and 1.1 moles 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 sulfur 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.

The cyanine dye represented by the general formula described hereinabove may be synthesized by the well known methods. Some examples are given below.

(1) The synthesis of 1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-trimethine-indocyanine perchlorate:

1-n-octyl-2,3,3-trimethyl-5-nitroindolenium iodide and ortho-ethyl formate are heated in acetic anhydride to obtain cyanine dye. Iodide in cyanine dye is anion-exchanged.

Melting point: 136–138° C. (decomposition).

$\lambda_{\max.}=569 \text{ m}\mu$ (in methanol).

(2) Synthesis of 1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-2,2'-pentamethine-indocyanine perchlorate:

1-n-octyl-2,3,3-trimethylindolenium iodide and propene dianil are heated and condensed in the presence of piperidine,

thus produced dye is anion-exchanged.

Melting point: 175–176° C. $\lambda_{\max.}=668 \text{ m}\mu$ (in methanol)

Indocyanine dye having alkyl group at the center of the methine chain may be obtained by using potassium acetate (alkyl= CH_3) instead of ortho-ethyl formate and α -phenylamido- γ -phenylimido- β -methylpropene hydrochloride (alkyl= CH_3) instead of propene dianil.

(3) Synthesis of 3,3'-di-n-octyl-6,6'-dinitro-2,2'-thiacarbocyanine-perchlorate:

Two mols of 2-methyl-6-nitrobenzthiazole prepared by nitration of 2-methylbenzthiazole and one mol of ortho-ethyl formate are condensed in the presence of pyridine and n-octyltosylate to obtain 3,3'-dioctyl-6,6'-dinitro-2,2'-thiacarbocyanine tosylate. The latter is then ion-exchanged with perchlorate anions.

(4) Synthesis of 3,3'-n-hexyl-6,6'-dibromo-2,2'-thiacyanineiodide:

2-methyl-6-bromobenzothiazole-n-hexyl iodide is heated in pyridine.

(5) 3,3'-di-n-decyl-6,6'-dichloro-2,2'-thiadicarbocyanine bromide:

This compound is obtained by condensation of two mols of 2-methyl-6-chloro-benzthiazole-n-decyl bromide and one mol of propene dianil in the presence of potassium acetate and acetic anhydride.

The cyanine dyes which are used in the present inven-

tion and easily obtained commercially or easily synthesized are as follows:

3,3'-di-n-octyl-6,6'-dinitro-2,2'-thiacyanine perchlorate;

3,3'-di-n-hexyl-6,6'-dinitro-2,2'-thiacyanine tosylate;

3,3'-di-n-octyl-6,6'-dinitro-2,2'-thiacarbocyanine perchlorate;

3,3'-di-n-nonyl-6,6'-dinitro-2,2'-thiadicarbocyanine perchlorate;

3,3'-dilauryl-6,6'-dichloro-2,2'-thiacarbocyanine bromide;

3,3'-dioctyl-5,6,5',6'-tetrachloro-thiacarbocyanine perchlorate;

3,3'-di-n-heptyl-6,6'-dibromo-2,2'-thiacyanine iodide;

3,3'-dioctyl-6,6'-dibromo-2,2'-thiacarbocyanine perchlorate;

3,3'-dihexyl-6,6'-dibromo-2,2'-thiadicarbocyanine tosylate;

3,3'-di(2-ethylhexyl)-6,6'-dibromo-2,2'-thiadicarbocyanine tosylate;

3,3'-di-n-decyl-5,5'-dichloro-6,6'-dinitro-thiacarbocyanine perchlorate;

3,3'-di-sec-hexyl-6,6'-dinitro-10-methyl-thiadicarbocyanine tosylate;

3,3'-di-sec-octyl-6,6'-dibrom-9-butyl-thiacarbocyanine tosylate;

1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-2,2'-trimethine-indocyanine perchlorate;

1,1'-di-n-hexyl-3,3,3',3'-tetramethyl-5,5'-dinitro-2,2'-trimethine-indocyanine tosylate;

1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-2,2'-pentamethineindocyanine perchlorate;

1,3,3,1',3',3'-hexamethyl-5,6,5',6'-tetrachloro-2,2'-trimethineindocyanine chloride;

1,1'-di-n-dodecyl-3,3,3',3'-tetramethyl-5,5'-dichloro-2,2'-trimethine-indocyanine perchlorate;

1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dibromo-2,2'-pentamethine-indocyanine bromide;

1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-diiodo-2,2'-trimethine-indocyanine perchlorate;

1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dichloro-10-methyl-2,2'-pentamethine-indocyanine chloride; and

1,1'-di-n-heptyl-3,3,3',3'-tetramethyl-5,5'-dibromo-9-methyl-2,2'-trimethine-indocyanine perchlorate.

In addition to the above, various derivatives may be obtained by exchange of anion functional groups with anions of other acids.

The photosensitive materials in accordance with the present invention may be provided in the following manner: An organic photoconductive compound and one of the cyanine dyes described above and if necessary an adhesive agent, plasticizer and other appropriate additives are dissolved or dispersed in a solvent, and then applied upon an electrically conductive support and dried.

Alternatively, the above compounds are melted and applied to a conductive support or a thin photosensitive film may be extruded from the solution or melt to provide a self-supporting film.

In addition to the cyanine dyes described above, the photosensitive materials may include an appropriate well known sensitizing dye such as crystal violet, malachite green, methylene blue, etc. (Reference is made to Yuki-gosei Kagaku Kyokaishi, Vol. 24, pages 1010–1027.) Furthermore, the chemical sensitizers such as Lewis acid; picric acid; 5-nitroacenaphthene; 2,4,7-trinitrofluorenone, maleic anhydride, chloroacetic acid, anthraquinone and the like, may be also added.

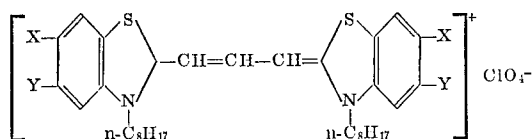
In accordance with the present invention, it is preferable to add to an organic photoconductive compound the cyanine dye in accordance with the present invention 0.01–2% in weight dissolved in a solvent such as methanol, acetone, chloroform, dimethylformamide, and the like.

The present invention will be more apparent from the following examples thereof, and it should be understood that the present invention is not limited by them.

11

Example 1

One gram of poly-9-vinylcarbazole (the trademark "Luvican M-170" from BASF Corp.) was dissolved in 20 ml. of special grade tetrahydrofuran, and 2.5×10^{-6} mol of cyanine dye represented by the following formula and dissolved in chloroform was added to prepare photo-sensitive solution.



X and Y are shown in Table 1-(1).

The photosensitive solution was applied upon high-grade paper treated with polyvinylalcohol, by use of a wirebar and dried to form a photosensitive layer of 5 microns in thickness. After the moisture content of the photosensitive paper was adjusted, it was charged and exposed by the Electrostatic Paper Analyzer manufactured by Kawaguchi Denki KK. And the exposure required to drop the initial as shown in Table 1-(2). The spectral sensitivity was measured by a spectrograph after it was charged.

TABLE 1-(1)

Dye number	X	Y	Melting point (° C.)	λ_{max}^1	Color of photosensitive paper
1-----	OCH ₃	H	94-95	575	Pink.
2-----	CH ₃	H	205	567	Do.
3-----	H	H	1245	558	Do.
4-----	Cl	H	203-204	563	Do.
5-----	Br	H	195-196	565	Do.
6-----	Cl	Cl	224-225	568	Do.
7-----	NO ₂	H	214-218	584	Blue.

¹ Absorption maxima in methanol in milli microns (m μ).

² Decomposition temperatures.

TABLE 1-(2)

Dye number	X	Y	Photo-sensitivity ¹	Spectral sensitivity ²
1-----	OCH ₃	H	1,000	596
2-----	CH ₃	H	795	590
3-----	H	H	510	580
4-----	Cl	H	325	590
5-----	Br	H	275	595
6-----	Cl	Cl	200	605
7-----	NO ₂	H	180	626

¹ Exposure (lux.sec.) required to drop the initial potential to 1/10.

² Maxima of spectral sensitivity in milli microns (m μ).

Dye Nos. 1-3 are not within the scope of the present invention and used for the purpose of comparison with the cyanine dyes of the present invention, dye Nos. 4-7. It is seen that the photosensitive papers utilizing the dyes 4-7 of the present invention have higher photosensitivity as compared with those of the prior art photosensitive papers even though the photosensitivity peaks are not so different. The spectral sensitivity curves of the photosensitive papers utilizing the dyes 4 and 7 are shown in FIGS. 2 and 3. Further, the relation of photosensitivity (E) and Hammett's substituent constant σ as shown in Table 1-(2) is illustrated in FIG. 1.

Example 2

Chlorinated poly-9-vinylcarbazole (with a chlorine content of 8.5%) -----grams-- 2
9-vinylcarbazole -----do----- 0.4
Carbon tetrabromide -----do----- 0.1
Benzene -----ml-- 20
Monochlorobenzene -----ml-- 20

The above compounds were uniformly mixed and dissolved and illuminated for 20 minutes by an ultra-high pressure mercury vapor lamp of 400 w. spaced apart by 20 cm. 0.01 gram of 3,3'-di-n-octyl-6,6'-dinitro-2,2'-thia-

12

carbocyanine perchlorate dissolved in 5 ml. of chloroform was added to the above solution to prepare the photosensitive solution. The photosensitive solution was applied upon a high-grade polyvinylalcohol-treated paper to form a coating 5 microns in thickness when dried. The photosensitive paper thus prepared was negatively charged, and a plate bearing a positive image was placed upon it while illuminated by light of 50 luxes from an enlarger. The latent image formed was developed with a wet developing agent, and a better-quality image was formed. The optimum quantity of light for exposure was 45 luxes second. In case of the photosensitive paper utilizing crystal violet as an optical sensitizing dye, the optimum exposure was 75 lux.sec.

Example 3

Brominated poly-9-vinylcarbazole (bromine content, 14.5%) -----grams-- 2
3,3'-dioctyl 6,6'-dinitro - 2,2' - thiadicarbocyanine perchlorate -----do----- 0.01
Monochlorobenzene -----ml-- 20

The above ingredients were uniformly mixed and dissolved to form a photosensitive solution. This photosensitive solution was coated on a triacetate film of 100 μ thick having a coating of conductive polymer No. 261 (trade name, supplied by Calgon Corp. in U.S.A.) (5 μ thick) to form a coating of 8 μ thick (when dried). The resulting film was charged, imagewise exposed and developed in a way similar to Example 2 to form positive images of good quality. The optimum exposure amount was 52 lux.sec.

Absorption maximum of the above-mentioned cyanine dye in methanol was 680 m μ and the sensitivity peak of the resulting photosensitive paper was 725 m μ .

Example 4

Poly-9-vinylcarbazole -----grams-- 2
9-vinylcarbazole -----do----- 0.2
Carbon tetrabromide -----do----- 0.1
Benzene -----ml-- 40

The solution was illuminated for five minutes in the manner described in Example 2. Thereafter 0.01 gram of 3,3'-di-n-octyl-6,6'-dinitro-2,2'-thiacyanine perchlorate in dimethylsulfoxide was added.

The photosensitive solution was applied upon the high-grade polyvinylalcohol-treated paper to form a photosensitive layer 5 microns in thickness when dried. The photosensitive paper was charged, exposed and developed in the similar manner as described in Example 2. The optimum image was obtained when the exposure was 150 lux.second.

The spectral sensitivity curve of this photosensitive paper is shown in FIG. 4. For the purpose of comparison, the curves of the photosensitive paper utilizing no cyanine dye is shown in FIG. 5. From FIGS. 4 and 5, it is seen that the sensitivity to blue light is remarkably increased. The absorption maximum of 3,3'-dioctyl-6,6'-dinitro-2,2'-thiacyanine perchlorate used in Example 4 was 447 millimicrons in methanol, and the maximum peak of the photosensitive paper, 475 millimicrons.

Example 5

High polymer organic photoconductive compounds -----grams-- 2
0.2% solution of 3,3'-di-n-decyl-6,6'-dinitro-2,2'-thiadicarbocyanine perchlorate in chloroform -----ml-- 5
Tetrahydrofuran -----ml-- 30

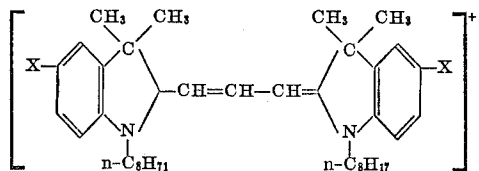
The above compounds were uniformly mixed and applied to a high-grade polyvinylalcohol-treated paper to form a coating 5 microns in thickness when dried. After the photosensitive paper was charged, a positive light image was projected to a photographic plate by using an enlarger having a xenon lamp as light source. The photosensitivity is shown in Table 2 following:

TABLE 2

High-polymer organic photoconductive compounds	Photo-sensitivity
Chlorinated poly-9-vinylcarbazole (chlorine content=24.8%)	65 lux.sec.
Poly-3-brom-6-chloro-9-vinylcarbazole	60 lux.sec.
Chlorinated-brominated-poly-9-vinylcarbazole (chlorine content=13.2%; bromine content=15.0%)	65 lux.sec.
Cyanated poly-9-vinylcarbazole (nitrogen content=9.65%)	55 lux.sec.
Thiocyanated poly-9-vinylcarbazole (sulfur content=7.18%)	70 lux.sec.

Example 6

One gram of poly-N-vinylcarbazole (sold under the trademark of "Luvican M-170" from BASF Corp.) was dissolved into 20 ml. of special grade tetrahydrofuran, and 0.1 mol of cyanin dyes represented by the following formula and dissolved into chloroform was added to prepare a photosensitive solution.



See Table 3 for X.

The sensitized solution was applied to a high-grade polyvinylalcohol-treated paper by use of a wire-bar to form a sensitized coating 6 microns in thickness when dried. After the moisture content was adjusted, the sensitized paper was charged and exposed by use of Electrostatic Paper Tester (Kawaguchi Denki KK.) to measure the exposure which dropped the initial voltage to $\frac{1}{10}$. The results were shown in Table 3. The spectral sensitivities after the sensitized paper was charged are also shown in Table 3.

TABLE 3

Dye number	X	λ_{max}^1	Color of photo-sensitive paper	Sensitivity ²	Sensitivity peak ³
1	H	551	Pink	250	570
2	Cl	556	do	135	575
3	Br	558	do	115	578
4	I	560	Red-violet	100	580
5	NO ₂	569	Blue-violet	75	590

¹ Absorption maxima (m μ) in methanol.

² Exposure (lux.sec.) required to drop the initial voltage to $\frac{1}{10}$.

³ Maximum spectral sensitivity (m μ).

The dye No. 1 was not the dye of the present invention and was tested for comparison. The photosensitive papers using the dyes Nos. 2-5 in accordance with the present invention have higher sensitivity than the photosensitive paper using the dye No. 1 even though the spectral sensitivity peaks are almost the same.

The spectral sensitivity curve of the photosensitive paper using the dye No. 5 is shown in FIG. 6.

Example 7

Chlorinated poly-9-vinylcarbazole (chlorine content=8.5%)	grams	2
9-vinylcarbazole	do	0.4
Carbon tetrabromide	do	0.1
Benzene	ml	20
Monochlorobenzene	ml	20

The above compounds were uniformly mixed and exposed for 20 minutes by a ultra-high pressure mercury vapor lamp, 450 w., spaced apart from the solution by 20 cm. Thereafter 0.01 gram of 1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-2,2'-trimethine-indocyanine perchlorate in 5 ml. of acetone was added to prepare the sensitized solution. The solution was then applied to a high-grade, polyvinylalcohol-treated paper to form a coating 5 microns in thickness when dried.

The sensitized paper was negatively charged and exposed with light of 500 luxes from an enlarger while a photographic plate bearing a positive image was made

in contact with the sensitized paper. The latent image was developed by a magnet brush process, and a good quality image was formed. The optimum exposure was 50 luxes.sec. while that for the sensitized paper prepared from the sensitized solution containing the same amount of crystal violet was 75 lux.sec.

Example 8

Chlorinated poly-9-vinylcarbazole (chlorine content: 12.5%)	grams	2
Chlorinated paraffin (chlorine content: 40%)	do	2
1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitro-pentamethine-indocyanine perchlorate	do	0.01
Methylene chloride	ml	20

The above-mentioned ingredients were uniformly mixed to form a photosensitive solution. The resulting photosensitive solution was coated on a triacetate film (100 μ thick) having a coating of conductive polymer No. 261 (trade name, supplied by Calgon Corp. in U.S.A.) of 5 μ thick to form a coating of 6 μ thick when dried. The resulting film was charged, imagewise exposed, and developed in a way similar to Example 7 to form positive images of good quality. The optimum exposure amount was 45 lux.sec. Absorption maximum of the above-mentioned cyanine dye in methanol was 668 m μ and the sensitivity peak of the resulting photosensitive paper was 685 m μ .

The spectral sensitivity curve is shown in FIG. 7.

Example 9

High polymer organic photoconductive compound	grams	2
1,1'-di-n-hexyl-3,3,3',3'-tetramethyl-5,5'-diiodo-2,2'-trimethine-indocyanine perchlorate (0.2% solution in dimethyl formamide)	ml	3
Tetrahydrofuran	ml	30

The above-mentioned ingredients were uniformly mixed and coated on a high quality paper to form a coating of 8 μ thick when dried. The resulting photosensitive paper was charged, imagewise exposed by an enlarger having a tungsten lamp as light source and developed to form a positive image. The sensitivity is shown in Table 4 below.

TABLE 4

High polymer organic photoconductor:	Photosensitivity, lux.sec.
Chlorinated poly-9-vinylcarbazole (chlorine content: 15.8%)	70
Poly-(3-bromo-6-chloro-9-vinylcarbazole)	65
Brominated poly-9-vinylcarbazole (bromine content: 20.5%)	65
Cyanated poly-9-vinylcarbazole (nitrogen content: 9.65%)	55
Thiocyanated poly-9-vinylcarbazole (sulfur content: 6.2%)	60

Example 10

Two grams of poly-3,6-dichloro-9-vinylcarbazole was dissolved into 30 ml. of monochlorobenzene, and then 5 ml. of 0.2% acetone solution of 1,1'-di-n-dodecyl-3,3,3',3'-tetramethyl-5,5'-dibrom-9-methyl-2,2'-trimethine-indocyanine perchlorate was added. The solution was applied to aluminum foil to form a coating of 7 microns in thickness when dried. The photosensitive plate was charged, exposed and developed with a liquid developing agent. The optimum exposure was 90 lux.sec., and the spectral sensitivity peak was 575 m μ .

Example 11

Photoconductor	grams	2
Polycarbonate	do	1
Methylene chloride	ml	30
1,1'-di-n-octyl-3,3,3',3'-tetramethyl-5,5'-dinitrotrimethineindocyanine tosylate	grams	0.006

The above-mentioned ingredients were uniformly mixed and dissolved, coated on a paper treated with polyvinyl alcohol to form a coating (7 μ thick when dried), and dried. On the other hand, a photosensitive paper not containing a sensitizing dye was separately prepared. After moistured, the photosensitive paper was charged by using an electrostatic paper analyzer (manufactured by Kawaguchi Denki) and exposed to a tungsten lamp and the exposure amount requiring decreasing the potential to 1/2 time the value of the initial potential was measured. The obtained value was converted to specific sensitivity. The result is listed in Table 5.

TABLE 5

	Non-sensitized photo-sensitive paper	Sensitized photo-sensitive paper
A-----	2	500
B-----	2.5	540
C-----	1	86
D-----	1	70
E-----	1	95

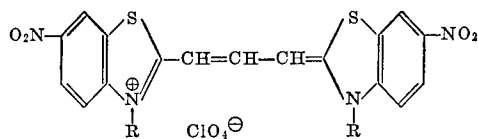
NOTE.—A=Poly-9-vinylcarbazole; B=Chlorinated poly-9-vinylcarbazole (chlorine content: 10.5%); C=4,4'-di-(dimethylamino) benzophenone; D=Bis-(4,4'-diallylamino)benzylidene) azine; E=N,N'-Dibenzyl-N,N'-diallyl-m-phenylenediamine.

Example 12

One gram of poly-9-vinylcarbazole (trademark, "Luvi-can M-170," supplied by BASF) was dissolved in 15 ml. of monochlorobenzene, and 0.5 g. of chlorinated paraffine (trademark, "Empara-40") was added thereto as plasticizer. To the resulting solution was added 2.5×10^{-6} mole of dye in a form of a solution of dye in dimethylsulfoxide (2 mg. dye/1 ml. dimethylsulfoxide). The resulting photosensitive solution was coated on a high quality paper having a coating of polyvinylalcohol to form a coating of 5 μ thick when dried by using a wire-bar and dried. The photosensitive paper was allowed to stand in a constant humid box of R.H. 60% for 2 days, then charged with an electrostatic paper analyzer (manufactured by Kawaguchi Denki), and exposed. Exposure amount required to decrease the potential to 1/2 time the initial potential was measured and listed below.

Spectral reflectivity of the same photosensitive paper was measured by using Beckmann Model BK-2A spectrophotometer. The peak of absorption wave length are described and compounds showing aggregation absorption are indicated below.

The chemical structure of dye used in this experiment is as follows:



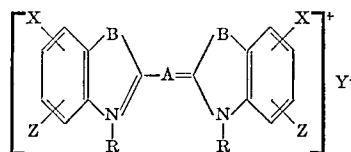
R	Photo-sensitivity (lux.sec.)	Absorption maxima (m μ)
C ₂ H ₅ -----	520	603
n-C ₄ H ₉ -----	280	607
n-C ₆ H ₁₃ -----	64	610
n-C ₈ H ₁₇ -----	22	614
n-C ₁₂ H ₂₅ -----	24	610

¹ Shoulder. ² Aggregation absorption.

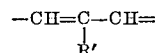
The above table clearly shows that cyanine dyes of C₂ and C₄ have photosensitivity lower than that of C₈ and C₁₂. FIG. 8 illustrates spectral reflectivity of compounds of the above formula where R is C₂H₅ or n-C₈H₁₇.

We claim:

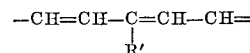
1. Organic photosensitive material for electrophotography which comprises a poly-9-vinylcarbazole or a derivative thereof and a cyanine dye of the formula



where A is a member selected from the group consisting of (CH=CH)_n-CH= where n is an integer of 0 to 2,



and



where R' is a lower alkyl containing 1 to 4 carbon atoms, B is —S— or >C(CH₃)₂; R is alkyl containing 6 to 12 carbon atoms; X and Z are each a substituent having Hammett's substituent constant δ of higher than +0.2 provided that one of X and Z may be hydrogen and Y is an anion, said cyanine dye being present in an amount from 0.01–2% by weight.

2. Organic photosensitive material for electrophotography according to claim 1 in which the photoconductor is a poly-9-vinylcarbazole derivative 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 brominated poly-9-vinylcarbazole chlorinated iodinated poly-9-vinylcarbazole, cyanated poly-9-vinylcarbazole, thiocyanated poly-9-vinylcarbazole, poly-3-methyl-9-vinylcarbazole, and chlorinated poly-3-methyl-9-vinylcarbazole.

3. Organic photosensitive material for electrophotography according to claim 1 in which R is a member selected from the group consisting of n-hexyl, sec-hexyl, n-heptyl, n-octyl, and 2-ethylhexyl.

4. Organic photosensitive material for electrophotography according to claim 1 in which X is nitro and Z is hydrogen.

5. Organic photosensitive material for electrophotography according to claim 1 in which X and Z are halogen.

6. Organic photosensitive material for electrophotography according to claim 1 in which X is nitro and Z is halogen.

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CHARLES E. VAN HORN, Primary Examiner