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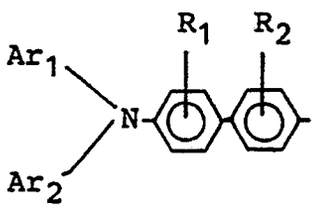
(71) Applicant: **CANON KABUSHIKI KAISHA**
30-2, 3-chome, Shimomaruko, Ohta-ku
Tokyo(JP)

(72) Inventor: **Senoo, Akihiro**
2-33-7 Aobadai Midori-ku
Yokohama-shi Kanagawa-ken(JP)
Inventor: **Yashiro, Ryoji**
563-1 Sobazuka Misakacho
Higashiyatsushiro-gun Yamanashi-ken(JP)
Inventor: **Kanemaru, Tetsuro**
2-13-4-404 Yayoi
Bunkyo-ku Tokyo(JP)
Inventor: **Kikuchi, Toshihiro**
7-1-16-205 Hiyoshi Kohoku-ku
Yokohama-shi Kanagawa-ken(JP)

(74) Representative: **Bühling, Gerhard, Dipl.-Chem. et al**
Patentanwaltsbüro Tiedtke-Bühling-Kinne
Grupe-Pellmann-Grams-Struif Bavariaring 4
D-8000 München 2(DE)

(54) Photosensitive member for electrophotography.

(57) A photosensitive member for electrophotography, including an electroconductive substrate and a photosensitive layer disposed thereon, wherein the photosensitive layer comprises a triarylamine compound represented by the following general formula (I):



(I),

wherein Ar_1 and Ar_2 respectively denote a benzene ring capable of having a substituent; at least one of Ar_1 and Ar_2 has an electron-donating substituent; and R_1 and R_2 respectively denote a hydrogen atom, alkyl or alkoxyl.

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PHOTOSENSITIVE MEMBER FOR ELECTROPHOTOGRAPHY

FIELD OF THE INVENTION AND RELATED ART

The present invention relates to a photosensitive member for electrophotography, particularly to a photosensitive member for electrophotography comprising a low-molecular weight organic photoconductor capable of providing improved electrophotographic characteristics.

Hitherto, there have been proposed a large number of organic photoconductive polymers to be used for electrophotographic photosensitive members, such as polyvinyl carbazole. These conventional organic polymers are superior to inorganic photoconductive materials in lightness (in weight), film-forming property, etc., but are inferior to the latter in sensitivity, durability, stability to environmental change, mechanical strength, etc.

On the other hand, there have been proposed several low-molecular weight organic photoconductive materials such as hydrazone compound (U.S. Patent 4,150,987), triaryl pyrazoline compound (U.S. Patent 3,837,851), and 9-styryl anthracene (Japanese Laid-Open Patent Application (JP-A, KOKAI) Nos. 94828/1976 and 94829/1976).

In a case where the conventional low-molecular weight organic photoconductors represented by those as described above are used, the above-mentioned defect in film-forming property, which has conventionally posed a problem in the field of the organic photoconductive polymer, may be obviated by appropriately selecting a binder to be used in combination therewith. However, these conventional organic photoconductors have not provide a sufficient sensitivity.

In such a viewpoint, there has recently been proposed a laminate-type structure wherein the photosensitive layer is function-separated into a charge generation layer and a charge transport layer. The electrophotographic photosensitive member comprising such a photosensitive layer may be improved in sensitivity to visible light, charge retentivity, surface strength, etc.

As the charge-transporting substance constituting the above-mentioned transport layer, a large number of organic compounds have heretofore been proposed. Examples thereof include: pyrazoline compounds (Japanese Laid-Open Patent Application No. 72231/1977), hydrazone compounds (U.S. Patent 842,431 and Japanese Laid-Open Patent Application No. 52063/1980), triphenylamine compounds (Japanese Laid-Open Patent Application Nos. 195254/1982 and 58445/1979), stilbene compounds (Japanese Laid-Open Patent Application Nos. 151955/1979 and 198043/1983), carbazole compounds (Japanese Laid-Open Patent Application Nos. 150128/1979 and 58451/1988), benzothiophene compounds (Japanese Laid-Open Patent Application No. 110835/1979), etc.

However, in the electrophotographic photosensitive member using the conventional low-molecular weight organic compound as the charge-transporting substance, the sensitivity and other electrophotographic characteristics are not necessarily sufficient, and the light part potential and dark part potential are liable to show a considerable change, when charging and exposure operations are conducted repetitively.

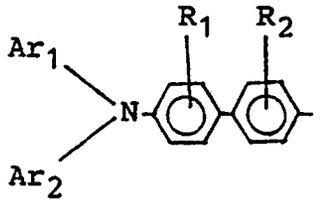
Accordingly, with respect to such an electrophotographic photosensitive member, there is still room for improvement.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an electrophotographic photosensitive member which has solved the above-mentioned various problems encountered in the conventional photosensitive member.

Another object of the present invention is to provide an electrophotographic photosensitive member using a novel organic photoconductor which may easily be produced, is relatively inexpensive and is excellent in durability.

According to the present invention, there is provided a photosensitive member for electrophotography, comprising an electroconductive substrate and a photosensitive layer disposed thereon, wherein the photosensitive layer comprises a triarylamine compound represented by the following general formula (I):



(I),

wherein Ar_1 and Ar_2 respectively denote a benzene ring capable of having a substituent; at least one of Ar_1 and Ar_2 has an electron-donating substituent; and R_1 and R_2 respectively denote a hydrogen atom, alkyl or alkoxyl.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 show infrared absorption spectra of Compound Example Nos. 10 and 13, respectively, according to the KBr tablet (or pellet) method.

DETAILED DESCRIPTION OF THE INVENTION

In the above general formula (I), Ar_1 and Ar_2 respectively denote a benzene ring capable of having one or more substituent. At least one of Ar_1 and Ar_2 has an electron-donating (or electron donative) group as a substituent. The "electron-donating substituent" used herein refers to a substituent having a greater electron-donating ability than a hydrogen atom.

Specific examples of the electron-donating group may include: alkyl groups (preferably C_1 to C_3) such as methyl, ethyl and propyl; alkoxyl groups (preferably C_1 to C_3) such as methoxy and ethoxy groups; substituted amino group (preferably, di-substituted amino group) such as dimethylamino and diethylamino groups; etc. The substituent of the amino group may preferably be C_1 to C_3.

R_1 and R_2 respectively denote a hydrogen atom, alkyl groups (preferably C_1 to C_3) such as methyl, ethyl and propyl; alkoxyl groups (preferably C_1 to C_3) such as methoxy and ethoxy.

Incidentally, it has heretofore been known that a triarylamine compound is used as a charge-transporting substance. However, in general, such a conventional triarylamine compound has provided a low sensitivity.

In the present invention, an electron-donating substituent is introduced into at least one of the benzene rings of Ar_1 and Ar_2 in the above-mentioned formula (I). As a result, according to the present invention, there is provided a charge-transporting substance which is capable of providing high sensitivity and high durability, and may easily be synthesized inexpensively, whereby the problems encountered in the prior art have been solved.

Particularly, a compound of the above-mentioned formula (I) having an oxidation potential of 0.9 V or below wherein at least one electron-donating group is introduced into the benzene ring of Ar_1 and/or Ar_2 may provide an excellent electrophotographic characteristic. Further, such a compound having an oxidation potential of 0.60 V or above and 0.88 V or below may provide an electrophotographic photosensitive member having an extremely high sensitivity.

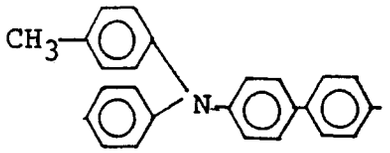
According to our investigation, it may be considered that the compound having an oxidation potential of above 0.9 V only provides insufficient carrier injection property from a charge-generation layer. On the other hand, the compound having an oxidation potential of below 0.60 V provides relatively large dark decay and relatively high residual potential to deteriorate the electrophotographic characteristic, while the reason for such a phenomenon is not necessarily clear.

Therefore, among the compounds represented by the above-mentioned general formula (I), a compound having an oxidation potential of 0.6 - 0.88 V wherein at least one of the benzene rings of Ar_1 and Ar_2 has an electron-donating substituent is particularly preferred since such a compound may provide an electrophotographic photosensitive member having excellent electrophotographic characteristics.

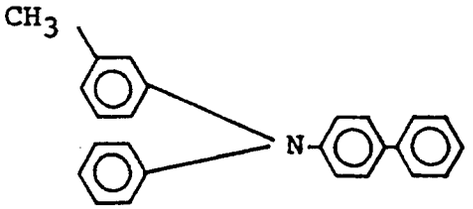
Representative examples of the compound of the above-mentioned formula (I) are described hereinbelow. However, the compound represented by the formula (I) usable in the present invention is not restricted to these specific examples.

In the following description, "E_{ox}" denotes an oxidation potential (volt).

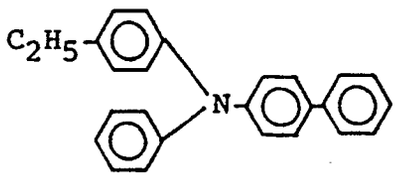
<Compound Examples>

1. 

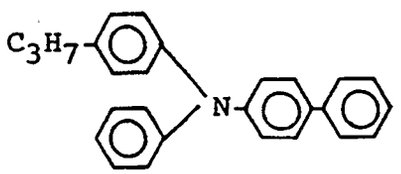
(E_{OX} = 0.87)

2. 

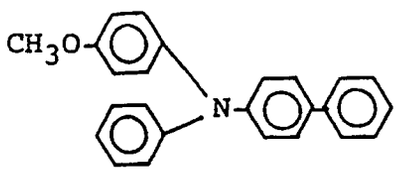
(E_{OX} = 0.88)

3. 

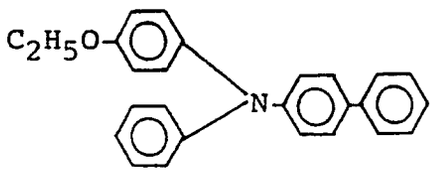
(E_{OX} = 0.86)

4. 

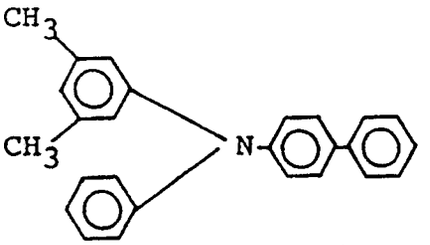
(E_{OX} = 0.86)

5. 

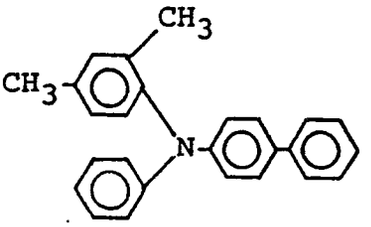
(E_{OX} = 0.81)

6. 

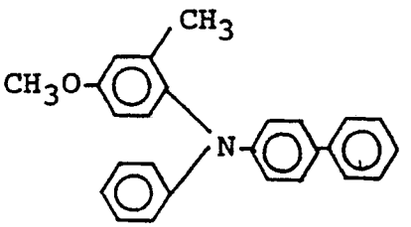
(E_{OX} = 0.86)

7. 

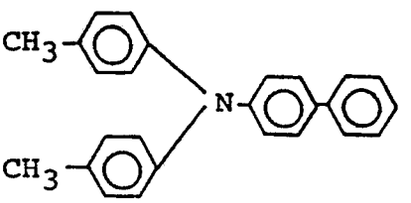
(E_{OX} = 0.87)

8. 

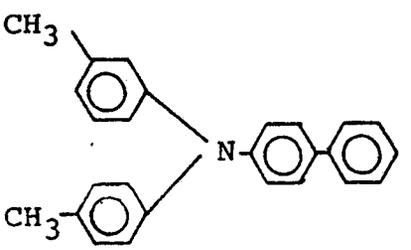
(E_{OX} = 0.85)

9. 

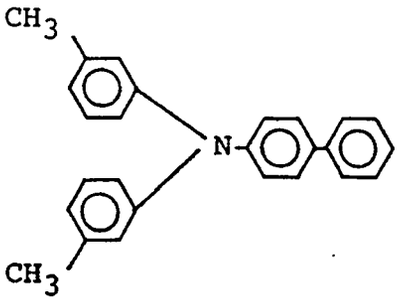
(E_{OX} = 0.78)

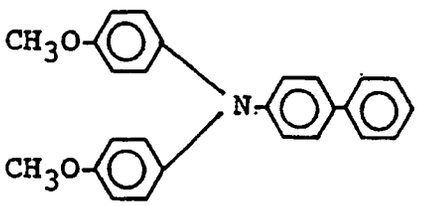
10. 

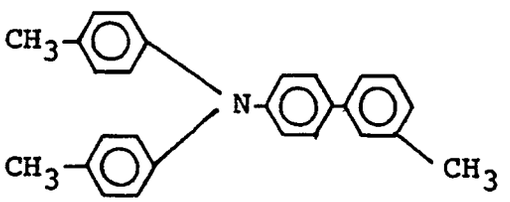
(E_{OX} = 0.86)

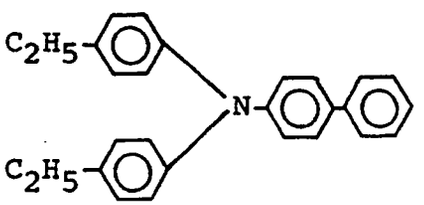
11. 

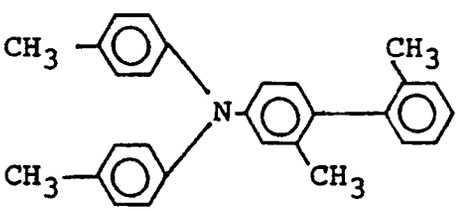
(E_{OX} = 0.86)

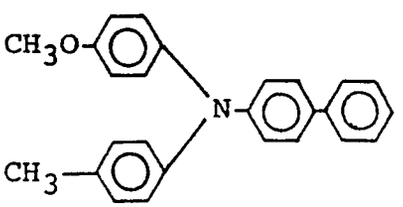
12.  (E_{OX} = 0.88)

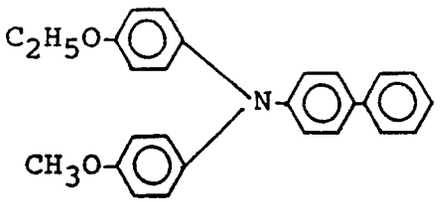
13.  (E_{OX} = 0.69)

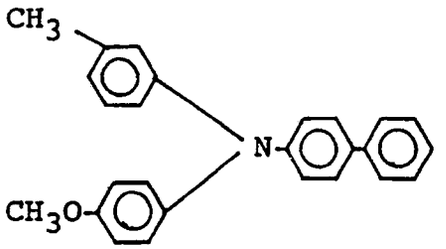
14.  (E_{OX} = 0.85)

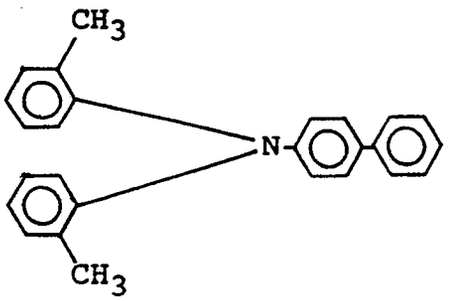
15.  (E_{OX} = 0.84)

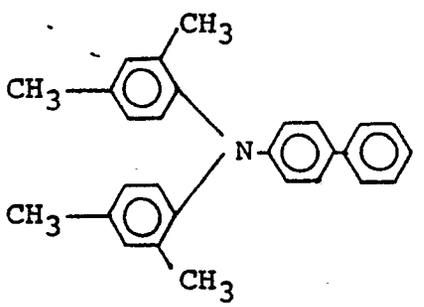
16.  (E_{OX} = 0.83)

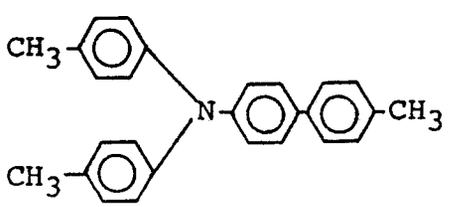
17.  (E_{OX} = 0.77)

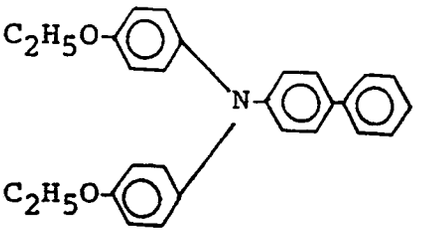
18.  (E_{OX} = 0.68)

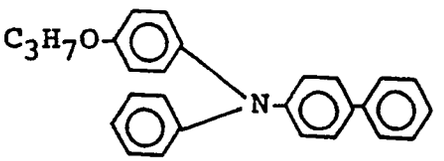
19.  (E_{OX} = 0.79)

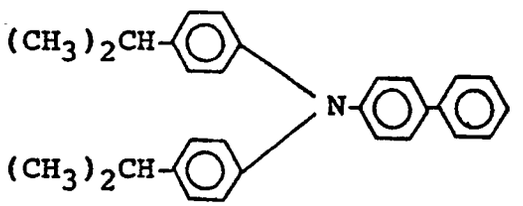
20.  (E_{OX} = 0.98)

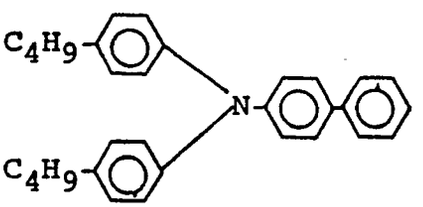
21.  (E_{OX} = 0.82)

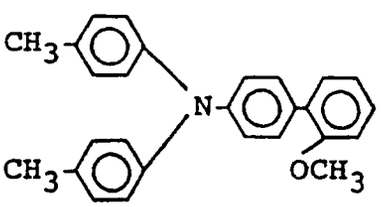
22.  (E_{OX} = 0.83)

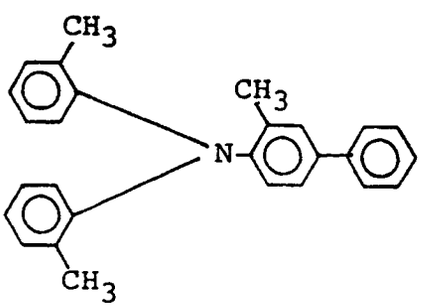
23.  (E_{OX} = 0.68)

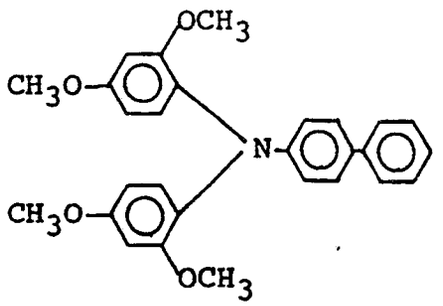
24.  (E_{OX} = 0.80)

25.  (E_{OX} = 0.87)

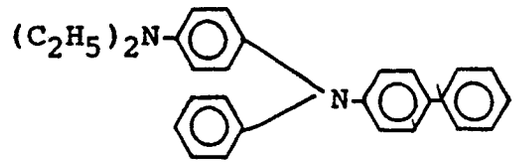
26.  (E_{OX} = 0.85)

27.  (E_{OX} = 0.82)

28.  (E_{OX} = 0.99)

29. 

(E_{OX} = 0.61)

30. 

(E_{OX} = 0.41)

Measurement of oxidation potential

The oxidation potential values referred to in the present invention are based on a measurement using a potential-sweeping method wherein a saturated calomel electrode was used as the reference electrode, and a 0.1 N solution of $(n\text{-}Bu)_4N^+ClO_4^-$ in acetonitrile was used as the electrolytic solution. In this measurement, the potential of the working electrode comprising platinum was swept to obtain a current-potential curve. The oxidation potential was defined as the potential value corresponding to the peak of the thus obtained current-potential curve.

More specifically, a sample was dissolved, at a concentration of about 5 - 10 mmol %, in an electrolytic solution of 0.1 N $(n\text{-}Bu)_4N^+ClO_4^-$ in acetonitrile. Then, a voltage was externally applied to the resultant sample solution, and a change in current was measured while linearly changing the voltage from a low potential value, thereby to obtain a current-potential curve. In this measurement, a counter electrode comprising platinum was used, and the potential (difference) between the working electrode and the counter electrode was measured while the potential (difference) between the reference electrode and the counter electrode was defined as 0 (zero). In the present invention, the oxidation potential was determined by the potential value corresponding to the peak of the current value in the above-mentioned current-potential curve.

The above-mentioend Compound Example may be synthesized in the following manner.

<Synthesis of Compound Example No. 10>

5.0 g (0.025 mol) of ditolylamine, 14.2 g (0.051 mol) of iodobiphenyl, 13.8 g (0.100 mol) of anhydrous potassium carbonate, 3.0 g of copper power (0.047 mol) and 50 ml of ortho-dichlorobenzene were charged in a three-necked 200 ml-flask equipped with a thermometer and a condenser, and were heated under stirring for 20 hours at a reflux temperature. After the reaction mixture was cooled, the solid content was removed from the reaction mixture by filtration, the filtrate was concentrated under reduced pressure, and then ethanol was added to the resultant product to obtain tan crystals of crude ditolylbiphenylamine.

The crude product was charged to a silica gel column and was developed by using a toluene-hexane solvent to obtain 6.8 g (yield = 77.9 %) of white crystals of purified ditolylbiphenylamine showing a melting point of 126.5 - 127.7 °C. Figure 1 shows an infrared absorption spectrum chart obtained by measuring the thus obtained compound by a KBr tablet (or pellet) method.

Elemental Analysis ($C_{26}H_{23}N$)			
	C(%)	H(%)	N(%)
Theoretical value	89.36	6.63	4.01
Observed value	89.40	6.61	3.99

Further, the above-mentioned Compound Example No. 13 was synthesized in a similar manner as described above. Figure 2 shows an infrared absorption spectrum chart obtained by measuring the thus obtained compound in the same manner as described above.

Since the compound according to the present invention may easily be synthesized in a high yield by using a one-step process as described above, it may provide an inexpensive electrophotographic photosensitive member.

The other compounds according to the present invention may be synthesized in a similar manner as described in the above Synthesis Example.

In a preferred embodiment of the present invention, the photosensitive layer is function-separated into a charge generation layer and a charge transport layer, and the charge transport layer comprises the triarylamine compound represented by the above-mentioned general formula (I) as a charge-transporting substance.

The charge transport layer according to the present invention may preferably be formed by dissolving the above-mentioned compound of the formula (1) in an appropriate solvent together with a binder, applying the resultant coating liquid such as solution onto a predetermined surface, and drying the resultant coating.

Examples of the binder to be used in the charge transport layer may include: polyarylate resins, polysulfone resins, polyamide resins, acrylic resins, acrylonitrile resins, methacrylic resins, vinyl chloride resins, vinyl acetate resins, phenol resins, epoxy resins, polyester resins, alkyd resins, polycarbonate, polyurethane, or copolymer resins containing two or more of the recurring units of these resins, such as styrene-butadiene copolymers, styrene-acrylonitrile copolymers, styrene-maleic acid copolymers, etc. Also, other than such insulating polymers, organic photoconductive polymers such as polyvinylcarbazole, polyvinylanthracene and polyvinylpyrene may be used.

In the charge transport layer, the charge-transporting substance may preferably be used in an amount of 10 - 500 wt. parts, more preferably 50 - 200 wt. parts, per 100 wt. parts of the binder.

The charge transport layer is electrically connected to the charge generation layer as described hereinafter, and has a function of receiving charge carriers injected from the charge generation layer in the presence of an electric field and of transporting these charge carriers to the surface of the charge transport layer. In such an embodiment, the charge transport layer may be disposed on the charge generation layer, or may be disposed under the charge generation layer. The charge transport layer may preferably be disposed on the charge generation layer. It is not preferred that the charge transport layer has too large a thickness, since there is a certain limit to the thickness thereof suitable for the transport of the charge carriers. In general, the charge transport layer may preferably have a thickness of 5 - 40 microns, more preferably 10 - 30 microns.

The organic solvent to be used in the above-mentioned formation of the charge transport layer may vary depending on the kind of the binder used therefor, and may preferably be selected from those which do not substantially dissolve the charge generation layer or a primer (or undercoat) layer as described hereinafter.

Specific examples of such an organic solvent may include: alcohols such as methanol, ethanol, and isopropanol; ketones such as acetone, methyl ethyl ketone, and cyclohexanone; amides such as N,N-dimethylformamide and N,N-dimethylacetamide; sulfoxides such as dimethyl sulfoxide; ethers such as tetrahydrofuran, dioxane, and ethylene glycol monomethyl ether; esters such as methyl acetate and ethyl acetate; aliphatic halogenated hydrocarbons such as chloroform, methylene chloride, dichloroethylene, carbon tetrachloride, and trichloroethylene; aromatic compounds such as benzene, toluene, xylene, monochlorobenzene, and dichlorobenzene; etc.

The coating may be effected by various coating methods such as dip coating, spray coating, wire bar coating, and blade coating. The drying should preferably be conducted in the sequence of drying at room temperature to a "tack-free" state and then heat drying. In general, the heat drying may preferably be conducted for a time in the range of 5 minutes to 2 hours at a temperature of 30 °C to 200 °C under quiescent condition or under blowing.

The charge transport layer according to the present invention can further contain an additive selected

from various species thereof. Examples of such an additive may include: plasticizers such as diphenyl, m-terphenyl and dibutyl phthalates; surface- lubricating agents such as silicone oil, graft-type silicone polymers, and various fluorocarbons; potential stabilizing agents such as dicyanovinyl compounds and carbazole derivatives; anti-oxidizing agents such as β-carotene, Ni complexes, and 1,4-diazabicyclo[2,2,2]-octane; etc.

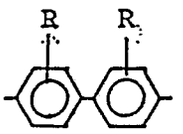
The charge generation layer may comprise a charge-generating substance. Specific examples of the charge-generating substance may include: inorganic charge-generating substances such as selenium, selenium-tellurium, and amorphous silicon; and organic charge-generating substances including: cationic dyes such as pyrylium dye, thiapyrylium dye, azulenium dye, thiacyanine dye, and quinocyanine dye; polycyclic quinone pigments such as squarium salt dye, phthalocyanine pigment, anthanthrone pigment, dibenzpyrene-quinone pigment, and pyranthrone pigment; indigo pigment; quinacridone pigment; azo pigment; etc. These charge-generating substances may be used singly or as a combination of two or more species. The charge generation layer may be formed by using such a charge-generating substance in the form of a vapor deposition layer or coating layer.

Among the above-mentioned charge-generating substances, the azo pigment particularly includes various types. Representative structures of the azo pigment preferably used in the present invention are described hereinbelow. When the azo pigment is represented by a general formula including the following central skeleton A:

$A\{N=N\text{-}Cp)_n$

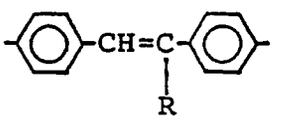
wherein Cp denotes a coupler portion (or coupler moiety) and n is 2 or 3, specific examples of the central skeleton A include those comprising the following structures:

A-1



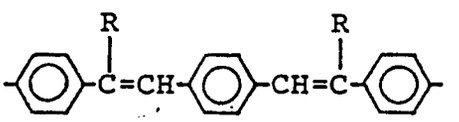
(R: H, Cl, OCH_3)

A-2



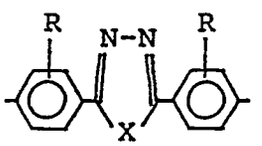
(R: H, CN)

A-3



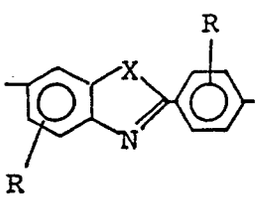
(R: H, CN)

A-4



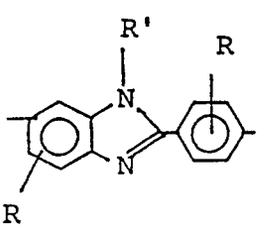
(X: O, S R: H, CH_3, Cl)

A-5



(X: O, S R: H, CH_3, Cl)

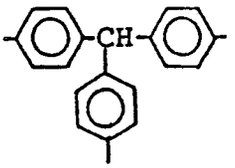
A-6



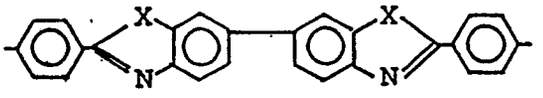
(R: H, CH_3, Cl,

R': H, CH_3, )

A-7

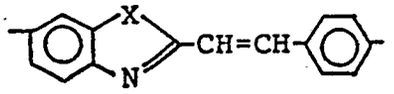


A-8



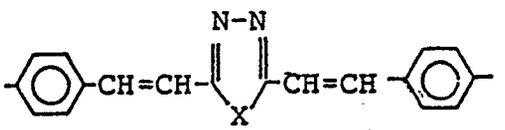
(X: O, S)

A-9



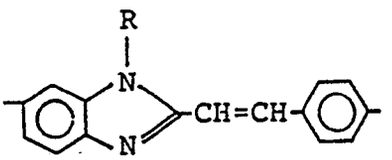
(X: O, S)

A-10



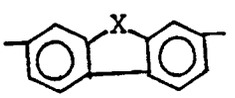
(X: O, S)

A-11



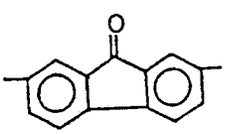
(R: H, CH_3)

A-12



(X: CH_2, O, S, SO_2

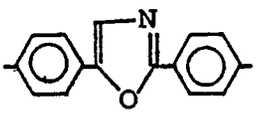
A-13



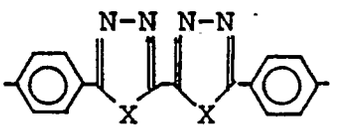
A-14

(X: O, S)

A-15

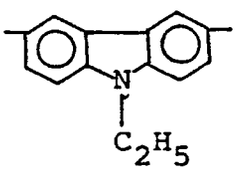


A-16

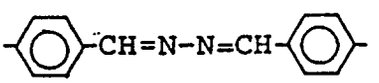


(X: O, S)

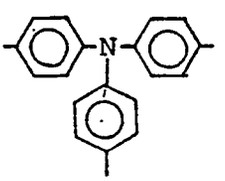
A-17



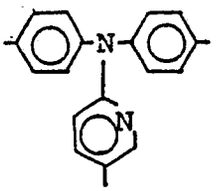
A-18



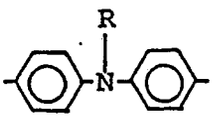
A-19



A-20

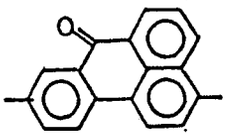


A-21



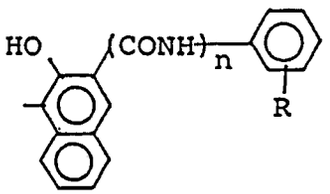
(R: H, CH_3)

A-22



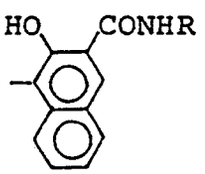
Specific examples of the coupler portion Cp include those having the following structures:

Cp-1



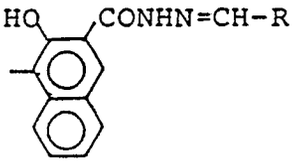
(R: H, halogen atom, alkoxy, alkyl, nitro group, etc.
n = 1 or 2)

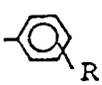
Cp-2



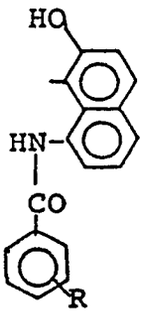
(R: CH_3, C_2H_5, C_3H_7)

Cp-3



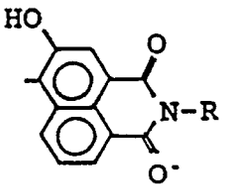
(R: alkyl or 
R' = H, halogen atom, alkoxy, alkyl, nitro group, etc.)

Cp-4

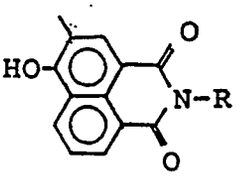


(R: H, halogen atom, alkoxyl, alkyl, nitro group, etc.)

Cp-5

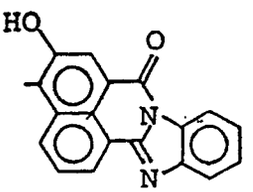


or

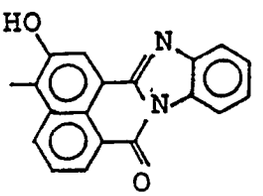


(R: alkyl, aryl, etc.)

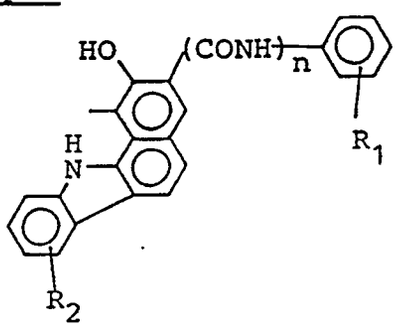
Cp-6



or



Cp-7



(R_1, R_2: H, halogen atom, alkoxy, alkyl, nitro group, etc.

n = 1 or 2)

The above-mentioned central structures A and coupler Cp may appropriately be combined to form a pigment as a charge-generating substance.

The charge generation layer may be formed by vapor-depositing such a charge-generating substance by means of a vacuum vapor deposition device, or by applying a dispersion containing such a charge-generating substance dispersed therein, together with an appropriate binder as desired.

The binder to be used for forming the charge generation layer may be selected from a wide variety of insulating resins or alternatively from organic photoconductive polymers such as polyvinylcarbazole, polyvinylanthracene, and polyvinylpyrene. There may preferably be used the insulating resin such as polyvinyl butyral, polyarylates (e.g., polycondensation product between bisphenol A and phthalic acid), polycarbonate, polyester, phenoxy resin, acrylic resin, polyacrylamide resin, polyamide, polyvinyl pyridine, cellulose resin, urethane resin, epoxy resin, casein, polyvinyl alcohol, and polyvinyl pyrrolidone.

The resin may preferably be contained in the charge generation layer in an amount of 5 - 80 wt. %, more preferably 10 - 40 wt. %.

Specific examples of the organic solvent usable in the coating of the charge generation layer may include: alcohols such as methanol, ethanol, and isopropanol; ketones such as acetone, methyl ethyl ketone, and cyclohexanone; amides such as N,N-dimethylformamide and N,N-dimethylacetamide; sulfoxides such as dimethyl sulfoxide; ethers such as tetrahydrofuran, dioxane, and ethylene glycol monomethyl ether; esters such as methyl acetate and ethyl acetate; aliphatic halogenated hydrocarbons such as chloroform, methylene chloride, dichloroethylene, carbon tetrachloride, and trichloroethylene; aromatic compounds such as benzene, toluene, xylene, monochlorobenzene, and dichlorobenzene; etc.

The charge generation layer may preferably contain the above-mentioned charge-generation substance in an amount as large as possible, so that it may provide a sufficient absorbance. Further, the charge generation layer may preferably be a thin layer having a thickness of 5 microns or below, more preferably 0.01 - 1 micron so that it may inject charge carriers generated therein into the charge transport layer within the lifetime of the charge carriers. This may be attributable to facts such that most of the incident light quantity may preferably be absorbed into the charge generation layer to generate a large number of charge carriers, and that the thus generated charge carriers may preferably be injected into the charge transport layer without deactivation due to recombination or trapping thereof.

The above-mentioned photosensitive layer having a laminate structure comprising a charge generation layer and a charge transport layer may be disposed on an electroconductive substrate.

The electroconductive substrate may be a substrate which per se has an electroconductivity such as those of aluminum, aluminum alloy, copper, zinc, and stainless steel; alternatively, the above-mentioned metal substrate or a substrate of a plastic coated with, e.g., a vacuum vapor-deposited layer of aluminum, aluminum alloy, indium oxide, tin oxide or indium oxide-tin oxide alloy, or a mixture of an electroconductive powder (such as aluminum powder, titanium oxide, tin oxide, zinc oxide, carbon black and silver particles) and an appropriate binder; a substrate of paper or plastic impregnated with electroconductive particles, or a plastic substrate coated with an electroconductive polymer layer. The electroconductive substrate may be in any form such as sheet, drum, etc.

Between the electroconductive substrate and the photosensitive layer, there can be formed a primer or undercoat layer having a barrier function and an adhesive function. The primer layer may comprise e.g., casein, polyvinyl alcohol, nitrocellulose, ethylene-acrylic acid copolymer, polyamide (e.g., nylon 6, nylon 66, nylon 610, copolymer nylon, alkoxymethylated nylon, etc.), polyurethane, gelatin, or aluminum oxide. The thickness of the primer layer should preferably be 0.1 - 5 microns, particularly 0.5 to 3 microns.

In the electrophotographic photosensitive member according to the present invention, a protective layer can further be disposed on the photosensitive layer. Such a protective layer may comprise a resin, or a resin and an electroconductive material dispersed therein.

In another embodiment of the present invention, a pigment or dye having a photoconductivity may be used as a sensitizer. Examples of such a dye or pigment include: the above-mentioned disazo pigment, pyrylium dye, thiapyrylium dye, selenapyrylium dye, benzopyrylium dye, benzothiapyrylium dye, naphthopyrylium dye, and naphthothiapyrylium dye, as described in U.S. Patent 3,554,745; 3,567,438; and 3,586,500.

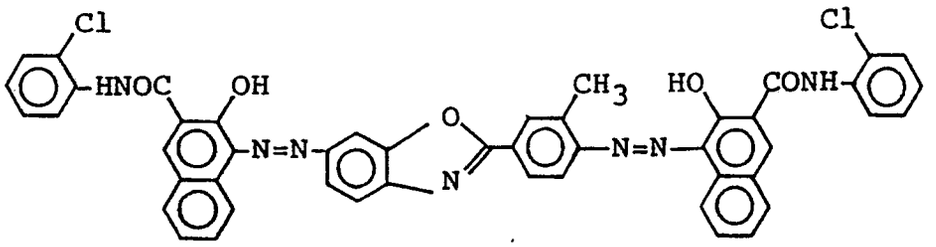
In a still another embodiment of the present invention, an euteclic (crystal) complex comprising a pyrylium dye (as disclosed in U.S. Patent 3,684,502) and an electrically insulating polymer comprising an alkylidene-diarylene portion may be used as a sensitizer. Such an eutectic complex may be formed by dissolving 4-[4-bis(2-chloroethyl)aminophenyl]-2,6-diphenylthiapyrylium perchlorate and poly(4,4′-isopropylidene diphenylene carbonate) in a halogenated hydrocarbon-type solvent (e.g., dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, chlorobenzene, bromobenzene, 1,2-dichlorobenzene, etc.), and then adding a non-polar solvent (e.g., hexane, octane, decane, 2,2,4-trimethylbenzene, ligroin, etc.) to the resultant mixture so as to produce a particulate eutectic complex. In such an embodiment, the electrophotographic photosensitive member may include a binder such as styrene-butadiene copolymer, silicone resin, vinyl resin, vinylidene chloride-acrylonitrile copolymer, styrene-acrylonitrile copolymer, vinyl acetate-vinyl chloride copolymer, polyvinyl butyral, polymethyl methacrylate, poly-N-butyl methacrylate, polyester, cellulose ester, etc.

The electrophotographic photosensitive member according to the present invention may be used not only for ordinary copying machines but also in the fields related to electrophotography such as laser printers, CRT printers and electrophotographic plate-making.

The present invention will be described in more detail with reference to Examples.

Example 1

5 g of a disazo pigment represented by the following formula:



and a solution obtained by dissolving 2 g of a butyral resin (butyral degree: 63 mol. %) in 100 ml of cyclohexanone were dispersed for 24 hours by means of a sand mill to prepare a coating liquid. The thus prepared coating liquid was applied onto an aluminum sheet by means of a wire bar to form a charge generation layer having a thickness (after drying) of 0.2 micron.

Then, 10 g of the above-mentioned Compound Example No. 3 and 10 g of a polycarbonate resin (weight-average molecular weight = 20,000) were dissolved in 70 g of monochlorobenzene to prepare a coating liquid. The coating liquid was applied onto the above-mentioned charge generation layer by means of a wire bar to form a charge transport layer having a thickness (after drying) of 20 microns, whereby an electrophotographic photosensitive member having a laminate structure was prepared.

The thus prepared photosensitive member was charged by using corona (-5 KV) according to a static method by means of an electrostatic copying paper tester (Model: SP-428, mfd. by Kawaguchi Denki K.K.) and retained in a dark place for 1 sec. Thereafter, the photosensitive member was exposed to light at an illuminance of 20 lux, to evaluate the charging characteristic. In order to evaluate the charging characteristic, the surface potential (V_0), the potential (V_1) obtained after a dark decay of 1 sec, and the exposure quantity ($E_{1/2}$) required for decreasing the potential V_1 to 1/2 thereof were measured.

Further, in order to measure the variations in light part potential and dark part potential in repetitive use, the photosensitive member prepared in this instance was bonded to the cylinder for a photosensitive drum to be used for a plain paper copying (PPC) machine (NP-3525, mfd. by Canon K.K.) and subjected to a copying test of 5000 sheets, and thereafter, the variations in the light part potential (V_L) and dark part potential (V_D) in the initial stage and after the copying of 5000 sheets were determined. The initial V_D and V_L were set to -700 V and -200 V, respectively.

The results are shown in the following Table 1.

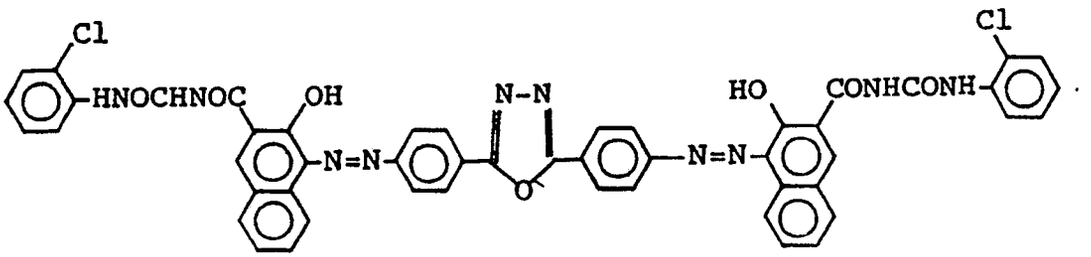
Table 1

	V_0 (V)	V_1 (V)	$E_{1/2}$ (lux.sec)	Initial potential (V)		Potential after copying of 5000 sheets (V)
Example 1	-700	-675	1.3	V_D	-700	-680
				V_L	-200	-207

Examples 2 - 10, Comparative Examples 1 - 3

Nine species of photosensitive members were prepared in the same manner as in Example 1 except that the above-mentioned Compound Examples (1), (5), (10), (13), (17), (20), (22), (28) and (30) were

respectively used as the charge-transporting substance instead of the Compound Example (13), and that a pigment having the following formula was used as the charge-generating substance (Examples 2 - 10).



The electrophotographic characteristics of the thus obtained photosensitive members were measured in the same manner as in Example 1.

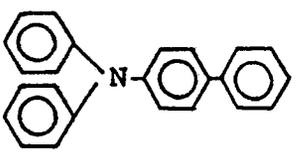
Further, for the purpose of comparison, three species of photosensitive members were prepared in the same manner as in Example 1 except that the following comparative compounds were respectively used as the charge-transporting substance (Comparative Examples 1 - 3).

The electrophotographic characteristics of the thus obtained photosensitive members were measured in the same manner as in Example 1.

The results are shown in the following Tables 2 and 3.

Comparative Compounds

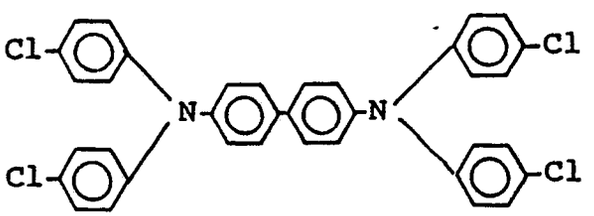
(1)



E_{OX} = 0.91 [V]

(disclosed in Japanese Laid-Open Patent Application No. 195254/1982)

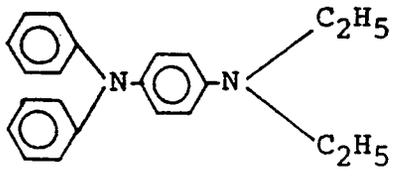
(2)



E_{OX} = 0.98 [V]

(disclosed in Japanese Laid-Open Patent Application No. 79450/1980)

(3)



E_{OX} = 0.40 [V]

(disclosed in Japanese Laid-Open Patent Application No. 195254/1982)

Table 2

Example	Compound Example	V_0 (V)	V_1 (V)	$E_{1/2}$ (lux.sec)	Initial potential		Potential after copying of 5000 sheets	
					V_D (V)	V_L (V)	V_D (V)	V_L (V)
2	(1) E_{OX}=0.87	-702	-690	1.2	-700	-200	-690	-225
3	(5) E_{OX}=0.81	-685	-680	1.3	-700	-200	-675	-205
4	(10) E_{OX}=0.86	-693	-690	0.8	-700	-200	-690	-205
5	(13) E_{OX}=0.69	-700	-695	0.9	-700	-200	-685	-215
6	(15) E_{OX}=0.84	-703	-695	0.8	-700	-200	-690	-207
7	(20) E_{OX}=0.98	-695	-673	2.1	-700	-200	-680	-205

...cont.

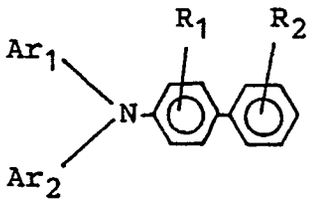
Table 2 (cont.)

8	(22) E_{OX}=0.83	-697	-692	1.2	-700	-200	-670	-215
9	(28) E_{OX}=0.99	-680	-650	2.3	-700	-200	-660	-215
10	(30) E_{OX}=0.41	-695	-630	2.9	-700	-200	-540	-235

Table 3

Comp. Example	Comp. Compounds	V_0 (V)	V_1 (V)	$E_{1/2}$ (lux.sec)	Initial potential		Potential after copying of 5000 sheets	
					V_D (V)	V_L (V)	V_D (V)	V_L (V)
1	1	-715	-690	3.4	-700	-200	-650	-300
2	2	-650	-600	6.2	-700	-200	-620	-325
3	3	-690	-632	5.4	-700	-200	-570	-375

As apparent from the above-mentioned results obtained in Examples and Comparative Examples, considerably high sensitivity and potential stability in successive copying may be realized by introducing a electron-donating substituent into Ar_1 and/or Ar_2 in the following formula:

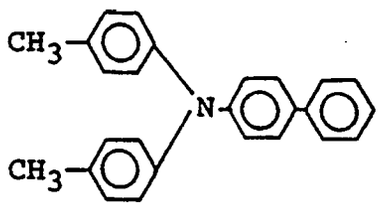


(I)

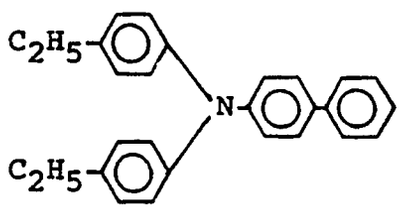
Particularly, when the results of Examples 2, 3 and 4 are compared with those of Comparative Example 1, the compounds used in the Examples have a structure similar to that used in Comparative Example 1, but the oxidation potentials of the Examples were decreased to 0.9 V or below due to the introduction of the electron-donating group. The compounds having an oxidation potential of 0.9 V or below clearly provided a high sensitivity, and excellent potential stability in successive copying.

Further, when a group having a considerably strong electron-donating property was introduced into Ar_1 and/or Ar_2 in the formula (I), there was observed a tendency that such a compound provided a somewhat lower sensitivity as compared with that provided by the compound having an oxidation potential of 0.60 - 0.88 V.

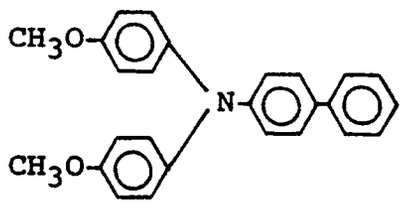
Among the compounds used in the above-mentioned Examples, the arylamine compounds represented by the following formulas (II), (III) and (IV) provided a particularly high sensitivity and an excellent potential stability in successive copying.



(II)



(III)



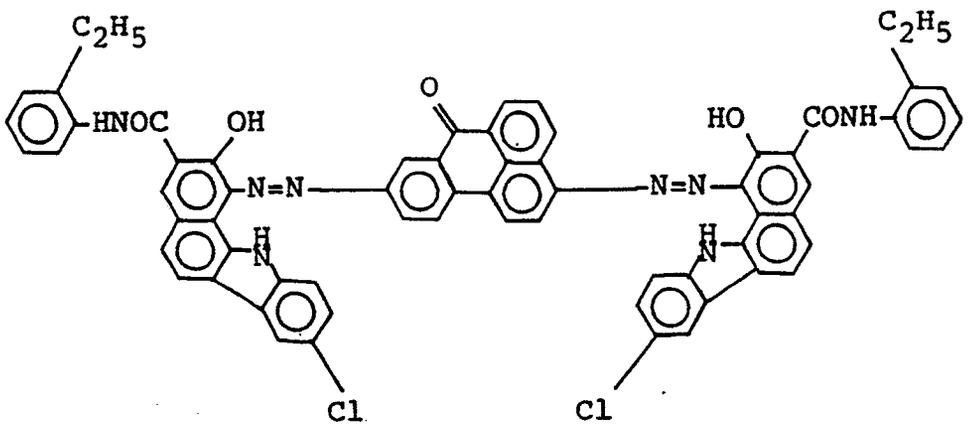
(IV)

Example 11

A coating liquid obtained by dissolving 5 g of a methoxymethylated nylon resin (number-average molecular weight = 32,000) and 10 g of an alcohol-soluble copolymer nylon resin (number-average molecular weight = 29,000) in 95 g of methanol was applied onto an aluminum substrate by means of a

wire bar to form a primer layer having a thickness of 1 micron (after drying).

Then, 10 g of a charge-generating substance represented by the following formula:



a solution obtained by dissolving 5 g of a butyral resin (butyral degree: 63 mol. %) and 200 g of dioxane were dispersed for 48 hours by means of a ball mill disperser to prepare a coating liquid. The thus prepared coating liquid was applied onto the above-mentioned primer layer by a blade coating method to form a charge generation layer having a thickness (after drying) of 0.15 micron.

Then, 10 g of the above-mentioned Compound Example No. 10 and 10 g of a polymethyl methacrylate resin (weight-average molecular weight = 50,000) were dissolved in 70 g of monochlorobenzene to prepare a coating liquid. The coating liquid was applied onto the above-mentioned charge generation layer by a blade coating method to form a charge transport layer having a thickness (after drying) of 19 microns, whereby an electrophotographic photosensitive member was prepared.

The thus prepared photosensitive member was charged by using corona discharge (-5 KV) so as to have an initial potential of V_0, left standing in a dark place for 1 sec, and thereafter the surface potential thereof was measured. In order to evaluate the sensitivity, the exposure quantity ($E_{1/2}$, $\mu J/cm^2$) required for decreasing the potential V_1 after the dark decay to 1/2 thereof was measured. The light source used herein was laser light (output: 5 mW, emission wavelength: 780 nm) emitted from a ternary semiconductor comprising gallium/aluminum/arsenic.

The results were as follows:

V_0: -700 V

V_1: -695 V

$E_{1/2}$: 0.53 $\mu J/cm^2$

The above-mentioned photosensitive member was assembled in a laser beam printer (trade name: LBP-CX, mfd. by Canon K.K.) as an electrophotographic printer equipped with the above-mentioned semiconductor laser using a reversal development system, and subjected to actual image formation.

The image formation conditions used herein were as follows:

surface potential after primary charging: -700 V
surface potential after image exposure: -150 V
(exposure quantity: 2.0 $\mu J/cm^2$)
transfer potential: +700 V
polarity of developer: negative
process speed: 50 mm/sec
developing condition (developing bias): -450 V
image exposure scanning system: image scan
exposure prior to the primary charging: 50 lux.sec
(whole surface exposure using red light)

The image formation was effected by line-scanning the laser beam corresponding to character and image signals. As a result, good prints were obtained with respect to the characters and images.

Further, when successive image formation of 3,000 sheets was conducted, good prints were stably obtained from the initial stage to 3,000 sheets.

Example 12

10 g of oxytitanium phthalocyanine was added to a solution obtained by dissolving 5 g of a phenoxy resin in 485 g of dioxane and dispersed for 2 hours by means of a ball mill. The thus prepared dispersion was applied onto an aluminum sheet by means of a wire bar and then dried at 80 °C for 2 hours to form a charge generation layer having a thickness of 0.5 micron.

Then, 10 g of the above-mentioned Compound Example No. 15 and 10 g of a bisphenol Z-type polycarbonate resin (weight-average molecular weight = 50,000) were dissolved in 70 g of monochlorobenzene to prepare a coating liquid. The coating liquid was applied onto the above-mentioned charge generation layer by means of a wire bar and then dried at 110 °C for one hour to form a charge transport layer having a thickness of 19 microns, whereby an electrophotographic photosensitive member was prepared.

The thus obtained photosensitive member was evaluated in the same manner as in Example 11. The results were as follows:

V_0: -695 V
V_1: -687 V
$E_{1/2}$: -0.69 μJ/cm^2

Example 13

3 g of 4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrilium perchlorate, 5 g of Compound Example No. 10 as a charge-transporting substance, and 5 g of a polyester resin (weight-average molecular weight = 49,000) were mixed with 50 g of a solvent comprising toluene and dioxane (1:1), and dispersed for 6 hours by means of a ball mill. The thus prepared dispersion was applied onto an aluminum sheet by means of a wire bar and then dried at 100 °C for 2 hours to form a photosensitive layer having a thickness of 15 microns, whereby an electrophotographic photosensitive member was prepared.

The thus obtained photosensitive member was evaluated in the same manner as in Example 1. The results were as follows:

V_0: -695 V V_1: -680 V
$E_{1/2}$: 1.9 lux.sec
(Initial stage)
V_D: -700 V
V_L: -200 V
(After copying of 5,000 sheets)
V_D: -680 V
V_L: -225 V

Example 14

An aqueous ammonia solution of casein (comprising 11.2 g of casein, 1 g of 28 % ammonia water, and 222 ml of water) was applied onto an aluminum plate by means of a wire bar to form a primer layer having a thickness of 1 micron (after drying). On the primer layer, a charge transport layer and a charge generation layer were successively formed in the same manner as in Example 9, whereby an electrophotographic photosensitive member was prepared in the same manner as in Example 1 except that the laminate structure was different.

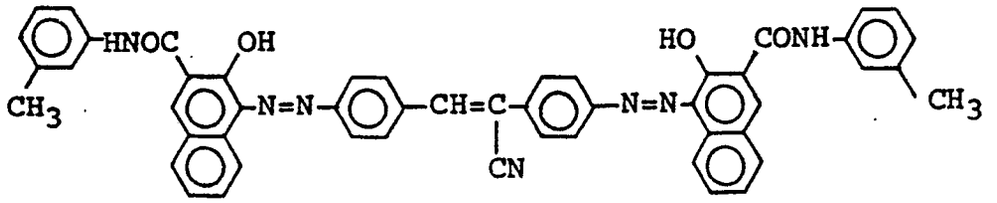
The charging characteristics of the thus obtained photosensitive member were evaluated in the same manner as in Example 1 except that the charging polarity was positive. The results were as follows:

V_0: + 695 V
V_1: + 670 V
$E_{1/2}$: 2.0 lux.sec

Example 15

A 5 % methanol solution of a soluble nylon (6-66-610-12 quaternary copolymer nylon) was applied onto an aluminum substrate to form a primer layer having a thickness of 0.5 micron (after drying).

Then, 5 of a pigment represented by the following formula:



was dispersed in 95 ml of tetrahydrofuran for 20 hours by means of a sand mill to prepare a dispersion.

Separately, 5 g of the above-mentioned Compound Example No. 28 and 10 g of a bisphenol Z-type polycarbonate resin (weight-average molecular weight = 50,000) were dissolved in 30 ml of monochlorobenzene to prepare a solution. The solution was then added to the above-mentioned dispersion, and further dispersed by means of a sand mill for 2 hours, thereby to prepare a coating liquid. The thus prepared coating liquid was applied onto the above-mentioned primer layer by means of a wire bar to form a photosensitive layer having a thickness of 20 microns (after drying), whereby an electrophotographic photosensitive member was prepared.

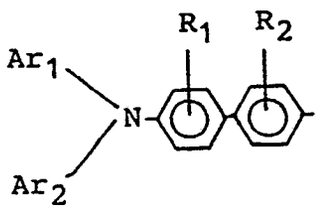
The electrophotographic characteristics of the thus obtained photosensitive member were evaluated in the same manner as in Example 1. The results were as follows:

V_0: -690 V

V_1: -675 V

$E_{1/2}$: 3.1 lux.sec

A photosensitive member for electrophotography, including an electroconductive substrate and a photosensitive layer disposed thereon, wherein the photosensitive layer comprises a triarylamine compound represented by the following general formula (I):

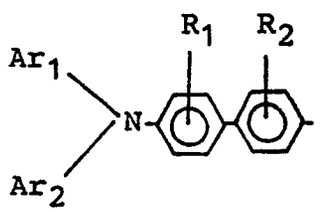


(I),

wherein Ar_1 and Ar_2 respectively denote a benzene ring capable of having a substituent; at least one of Ar_1 and Ar_2 has an electron-donating substituent; and R_1 and R_2 respectively denote a hydrogen atom, alkyl or alkoxyl.

Claims

1. A photosensitive member for electrophotography, comprising an electroconductive substrate and a photosensitive layer disposed thereon, wherein the photosensitive layer comprises a triarylamine compound represented by the following general formula (I):



(I),

wherein Ar_1 and Ar_2 respectively denote a benzene ring capable of having a substituent; at least one of Ar_1 and Ar_2 has an electron-donating substituent; and R_1 and R_2 respectively denote a hydrogen atom, alkyl or alkoxyl.

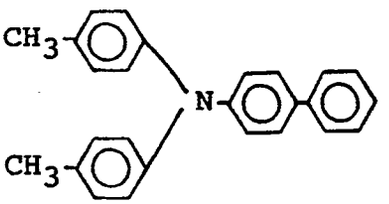
2. A member according to Claim 1, wherein the triarylamine compound represented by the formula (I)

has an oxidation potential of 0.90 V or lower.

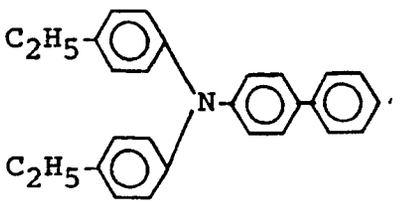
3. A member according to Claim 1, wherein the triarylamine compound represented by the formula (I) has an oxidation potential of not lower than 0.60 V and not higher than 0.88 V.

4. A member according to Claim 1, wherein at least one of Ar_1 and Ar_2 of the formula (I) has an electron-donating substituent selected from the group consisting of an alkyl, an alkoxyl and a substituted amino group.

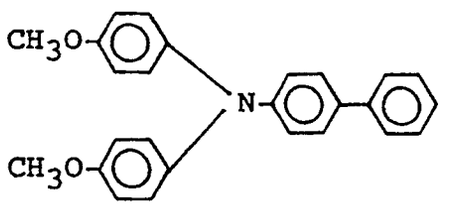
5. A member according to Claim 1, wherein the triarylamine compound represented by the formula (1) is a compound selected from the group consisting of the following compounds (II), (III) and (IV):



(II),



(III), and



(IV)

6. A member according to Claim 1 or 5, wherein the photosensitive layer has a laminate structure comprising a charge generation layer and a charge transport layer.

7. A member according to Claim 6, which comprises the electroconductive substrate, and the charge generation layer and the charge transport layer in this order on the substrate.

8. A member according to Claim 6, which comprises the electroconductive substrate, and the charge transport layer and the charge generation layer in this order on the substrate.

9. A member according to Claim 6, wherein the charge transport layer comprises a compound selected from the group consisting of those represented by the formulas (I), (II), (III) and (IV); and an insulating polymer or organic photoconductive polymer.

10. A member according to Claim 6, wherein the charge transport layer comprises a compound selected from the group consisting of those represented by the formulas (I), (II), (III) and (IV); an insulating polymer or organic photoconductive polymer; and at least one species selected from the group consisting of a plasticizer, a surface lubricating agent, a potential stabilizing agent, and an anti-oxidizing agent.

11. A member according to Claim 6, wherein the charge generation layer comprises an organic charge-generating substance and an insulating resin.

12. A member according to Claim 11, wherein the organic charge-generating substance comprises an azo pigment.

13. A member according to Claim 1 or 5, which further comprises a primer layer disposed between the electroconductive substrate and photosensitive layer.

14. A member according to Claim 1 or 5, which further comprises a protective layer disposed on the photosensitive layer.

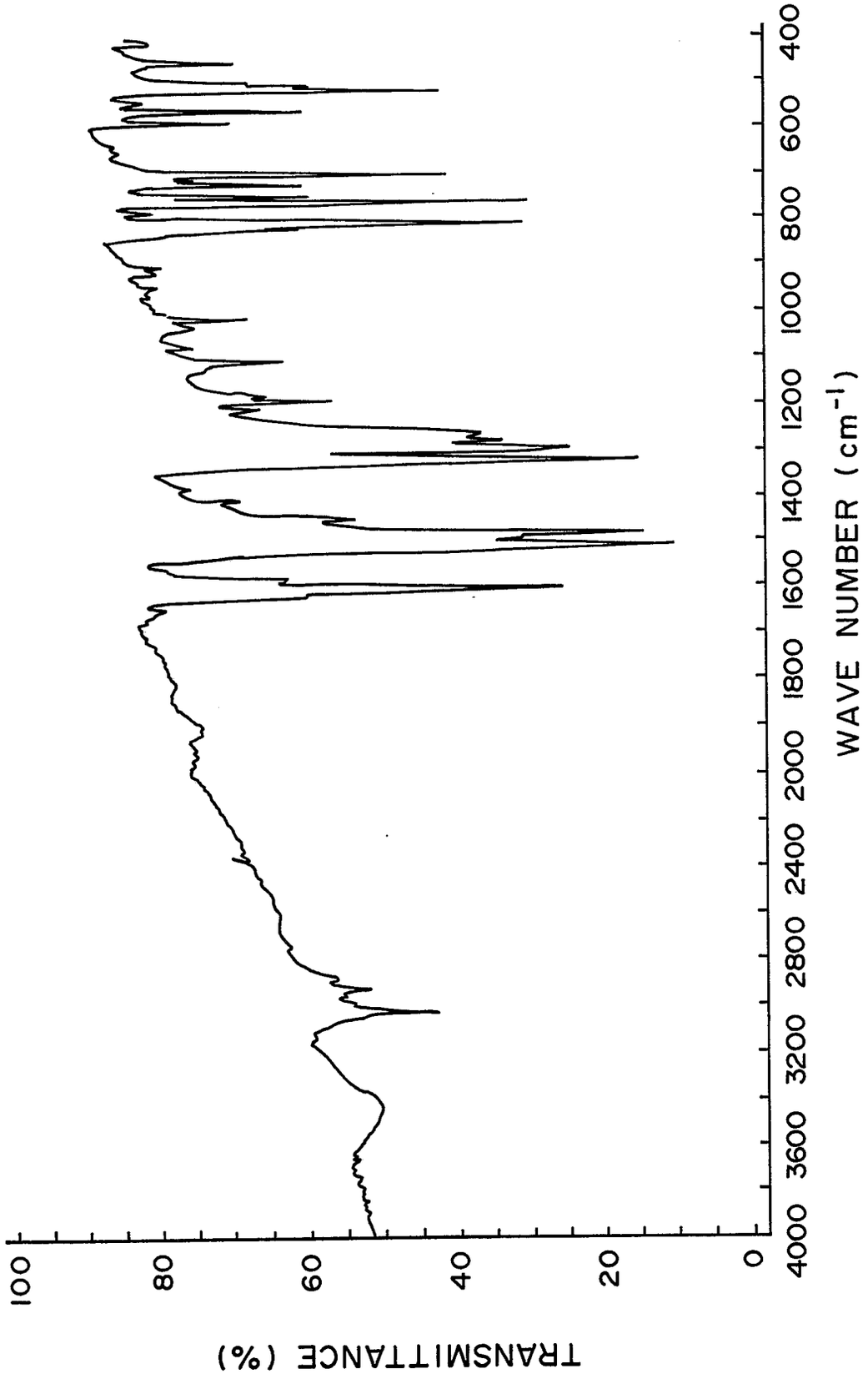

TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm⁻¹)

FIG. 1

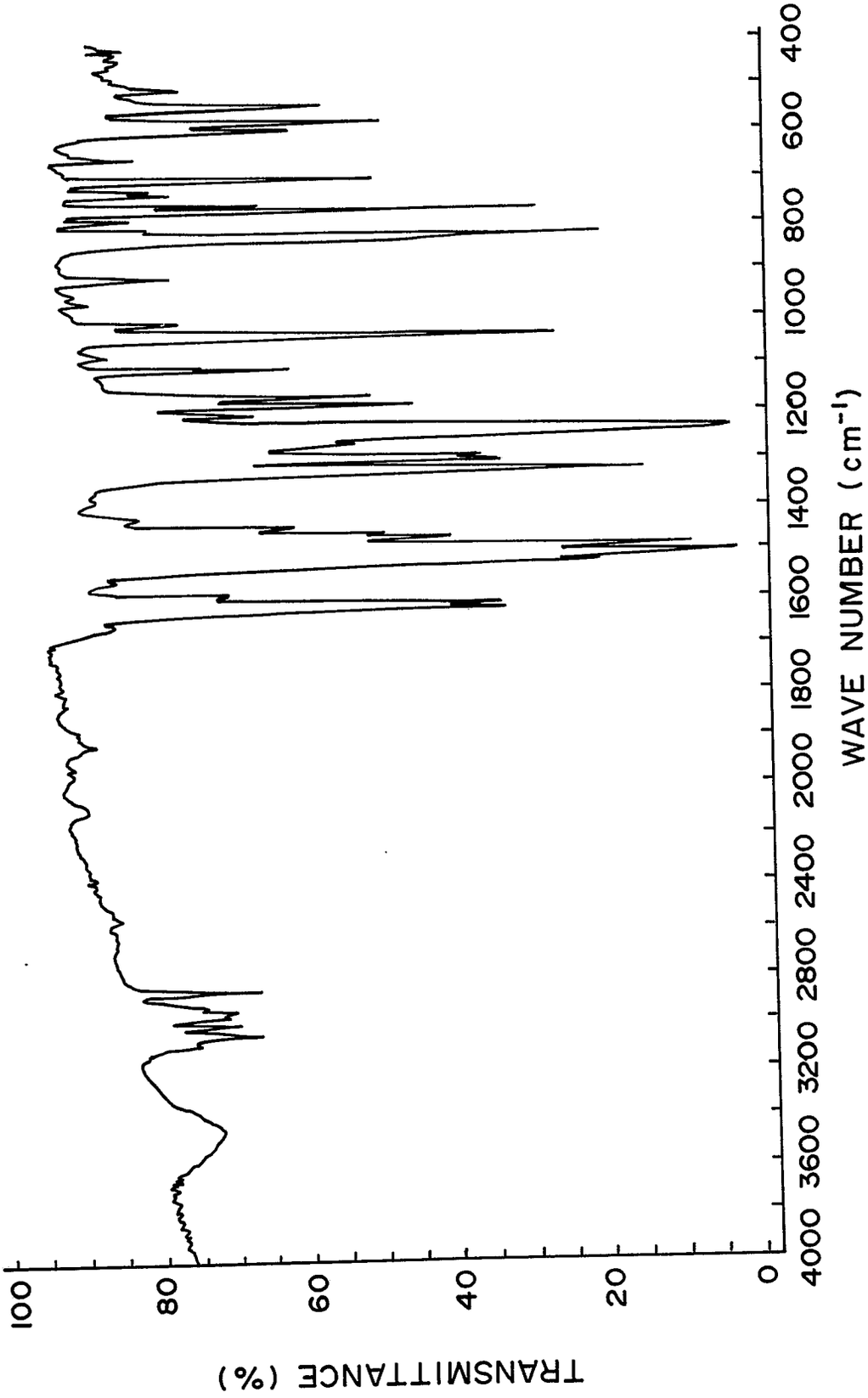

TRANSMITTANCE (%)
100
80
60
40
20
0
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
WAVE NUMBER (cm⁻¹)

FIG. 2