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(54) Electrophotographic lithographic printing plate.

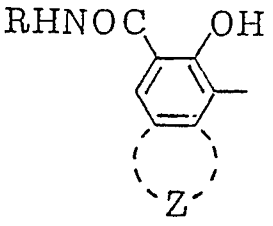
(57) The present invention provides an electrophotographic material for making lithographic printing plates which comprises an electrically conductive and hydrophilic base and, provided thereon, a photoconductive layer, said photoconductive layer comprising:

a resin binder soluble in at least one member selected from the group consisting of an alkali and an alcohol,

an azo compound heat treated in an organic solvent excluding alcohol solvent and represented by the following formula (I):

$Cp_1 - N = N - A - N = N - Cp_2$ (I)

wherein A represents a divalent residue which bonds through its C atom to N atoms which constitute azo, Cp_1 and Cp_2 are identical or different and Cp_1 is a group represented by the formula:



wherein Z represents a group of atoms necessary to form a substituted or unsubstituted carbocyclic aromatic ring, a substituted or unsubstituted heterocyclic aromatic ring or an unsaturated monocyclic hydrocarbon ring and R represents an aryl group having one or two CF_3 groups and

a carrier transport material.

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ELECTROPHOTOGRAPHIC LITHOGRAPHIC PRINTING PLATE

BACKGROUND OF THE INVENTION

The present invention relates to a lithographic printing plate and in particular to a lithographic printing plate made by electrophotography.

Hitherto, as photosensitive materials for making lithographic printing plates there have been known those which use photosensitive resins and silver halide photosensitive materials, but these have the problems that the former are low in sensitivity though high in resolution and printing endurance and the latter are expensive and inferior in printing endurance though high in sensitivity and resolution.

Lithographic printing plate materials of electrophotographic type having photoconductive materials are relatively high in sensitivity and can afford inexpensive printing materials of high printing endurance and have intensively been studied. Printing plates of this type are made by forming a photoconductive layer on a support and forming electrophotographically a toner image and hydrophilizing or dissolving away non-image portion. For example, in the case of a plate material comprising a support and, coated thereon, a photoconductive layer comprising a binder containing zinc oxide as a photoconductive material and a sensitizer, non-image portion is hydrophilized with potassium ferrocyanide to make a lithographic printing plate, but hydrophilicity of the non-image portion is poor and so print is apt to be stained and printing endurance is low. There is another material in which a hydrophilic aluminum sheet is used as a support and non-image portion is dissolved away, but in this case, photoconductive layer contains zinc oxide in a large amount and hence dissolution is difficult and the hydrophilic aluminum surface cannot be sufficiently utilized. Furthermore, in an example which uses organic photoconductors as photoconductive materials as disclosed in Japanese Patent Kokai (Laid-Open) No. 56-107246, a photoconductive layer comprising a binder soluble in an aqueous alkali or alcohol solution to which a large amount of oxadiazole organic photoconductor and a small amount of sensitizing dye are added is coated on an aluminum sheet. In this case, since oxadiazole photoconductor is contained in a large amount, dissolving-away is not necessarily effectively performed and oxadiazole photoconductor is often separated and precipitated and besides, sensitivity is low. In order to solve these problems, there has been proposed to make a photoconductive layer comprising two layers of carrier generation layer and carrier transport layer for improving sensitivity by reducing content of organic photoconductor, whereby sensitivity has been considerably enhanced. However double- layer constitution is employed and production cost increase.

Another example is to use a photoconductive layer comprising a binder soluble in aqueous alkali or alcohol solution in which organic photoconductive pigment is dispersed.

For example, in case of a material comprising an aluminum sheet on which is provided a photoconductive layer comprising a dispersion of phthalocyanine pigment in a phenolic resin, remarkable improvement in sensitivity cannot be expected and hence oxadiazole, pyrazoline and hydrazone photoconductors are added, which cause reduction of charged potential, separation of photoconductor and deterioration of property of dissolving-away of non-image portion. According to Japanese Patent Kokai (Laid-Open) No. 56-146135, there is provided a photosensitive layer containing a condensed polycyclic quinone pigment and an oxadiazole derivative as organic photoconductors in an alkali-soluble acrylic resin. However, this material is still insufficient in sensitivity and there is the possibility of precipitation of oxadiazole.

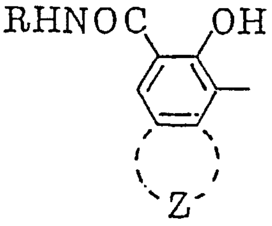
SUMMARY OF THE INVENTION

The object of the present invention is to provide a lithographic printing plate material which is free from the above defects, improved in pre-exposure properties, has high sensitivity, easy in dissolving away of non-image portion, less in printing stain and high in printing endurance.

The above object can be attained by printing plate made by forming a toner image by electrophotographic method on a printing plate material comprising an electrically conductive and hydrophilic base and, provided thereon, a photoconductive layer and thereafter dissolving away non-image portion other than the toner image portion with a solution mainly composed of an alkali and/or alcohol, characterized in that said photoconductive layer contains an alkali and/or alcohol soluble resin binder, an azo compound heat treated in an organic solvent excluding alcohol solvent and represented by the following formula (I):

$Cp_1 = N = N - A - N = N - CP_2$ (I)

[wherein A represents a divalent residue which bonds through its C atom to N atoms which constitute azo, Cp_1 and Cp_2 are identical or different and at least Cp_1 is a group represented by the formula:



(wherein Z represents a group of atoms necessary to form a substituted or unsubstituted carbocyclic aromatic ring, a substituted or unsubstituted heterocyclic aromatic ring or an unsaturated monocyclic hydrocarbon ring and R represents an aryl group having one or two CF_3 groups)], and a carrier transport material.

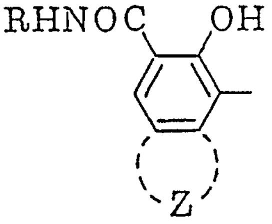
DESCRIPTION OF THE INVENTION

The first component which constitutes the photoconductive layer of the electrophotographic lithographic printing plate of the present invention is a resin binder soluble in alkali and/or alcohol. Hitherto, as these resin binders, there have been known, for example, phenolic resin, alcohol-soluble nylon resin, styrene-maleic anhydride copolymer, vinyl acetate-crotonic acid copolymer, vinyl acetate-maleic anhydride copolymer, and bipolymers or terpolymers of acrylic acid, methacrylic acid, crotonic acid or itaconic acid with styrene, acrylic acid ester or methacrylic acid ester.

The second component of the photoconductive layer of the present invention is an azo compound (pigment) represented by the formula (I) and heat treated in an organic solvent.

$Cp_1 - N = N - A - N = N - CP_2$ (I)

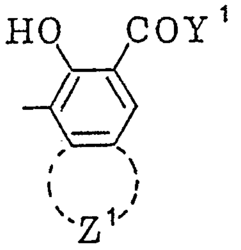
[wherein A represents a divalent residue which bonds through its C atom to N atoms which constitute azo, Cp_1 and Cp_2 are identical or different and at least Cp_1 is a group represented by the formula:



(wherein Z represents a group of atoms necessary to form a substituted or unsubstituted carbocyclic aromatic ring, a substituted or unsubstituted heterocyclic aromatic ring, or an unsubstituted monocyclic hydrocarbon ring and R represents an aryl group having one or two CF_3 groups)].

When Cp_2 is a coupler residue different from Cp_1, Cp_2 can be selected from the following formulas (a)-(f):

(a)



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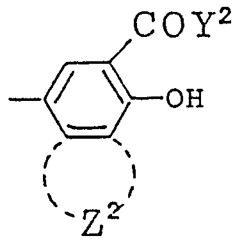

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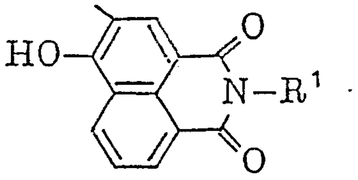
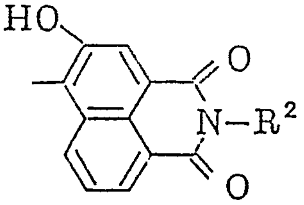
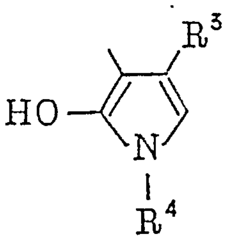


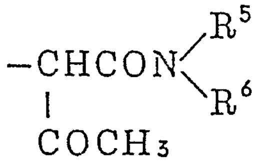
(d)



(e)



(f)

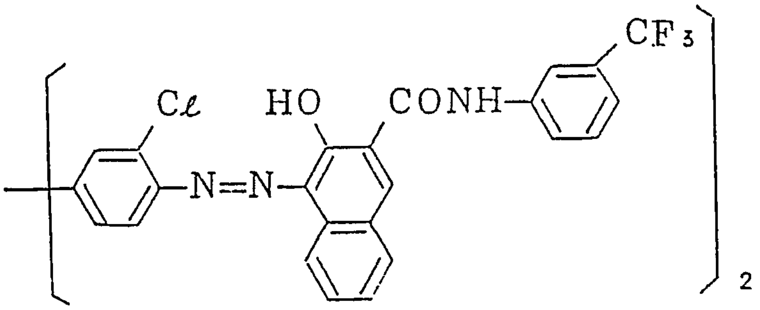


$$-\underset{\displaystyle COCH_3}{\underset{|}{CH}}CON\begin{matrix}R^5\\ R^6\end{matrix}$$

In the above formulas, Z^1 and Z^2 each represents a group of atoms necessary to form a substituted or unsubstituted aromatic hydrocarbon ring or a substituted or unsubstituted heterocyclic ring, R^1 and R^2 each represents a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group, R^3 represents an alkyl group or a carboxyl group or an ester thereof, R^4 and R^6 each represents a substituted or unsubstituted aryl or heterocyclic group, R^5 represents a hydrogen atom or a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group, and Y^1 and Y^2 each represents $-NR^7R^8$, $-OR^9$, $-NHN=CH-R^{10}$ or $-NHNR^{11}R^{12}$ wherein R^7, R^8, R^9, R^{11} and R^{12} each represents a hydrogen atom or a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group and R^{10} represents a substituted or unsubstituted aryl or heterocyclic group.

Nonlimiting examples of azo compounds represented by the formula (I) and useful in the present invention are shown below.

(1)



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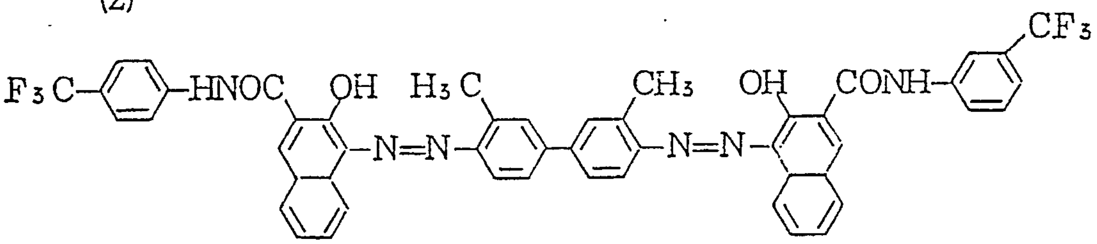

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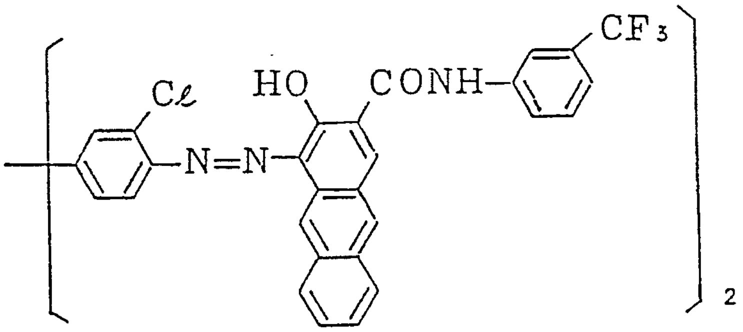

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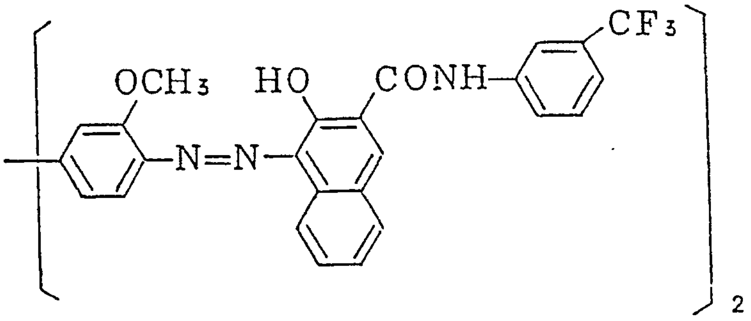

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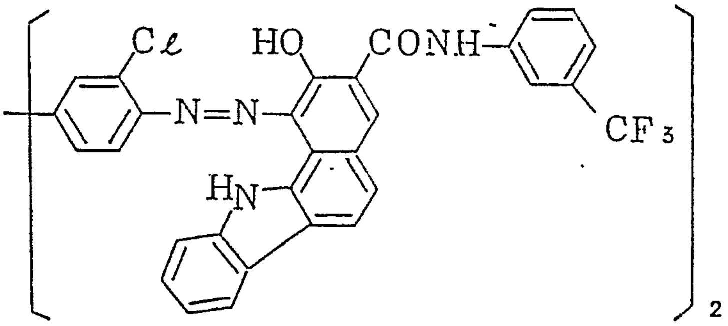

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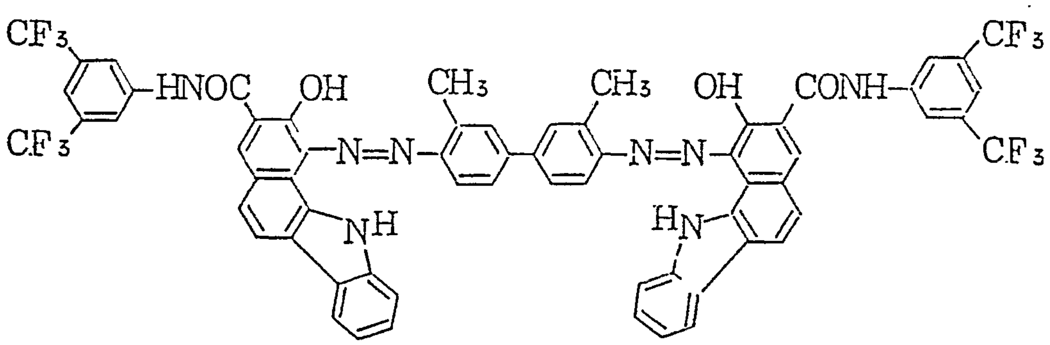

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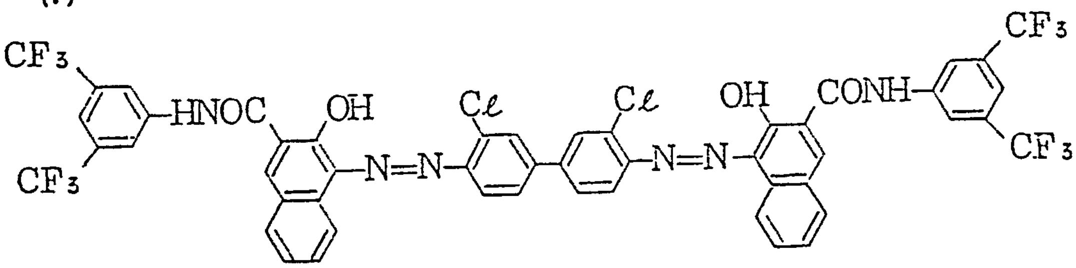

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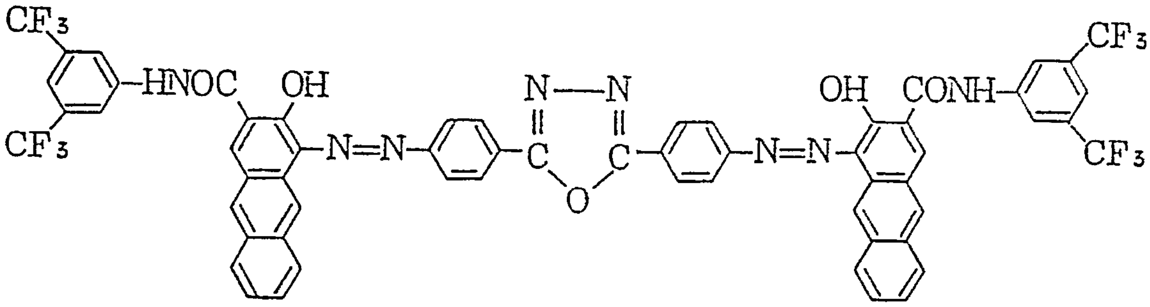

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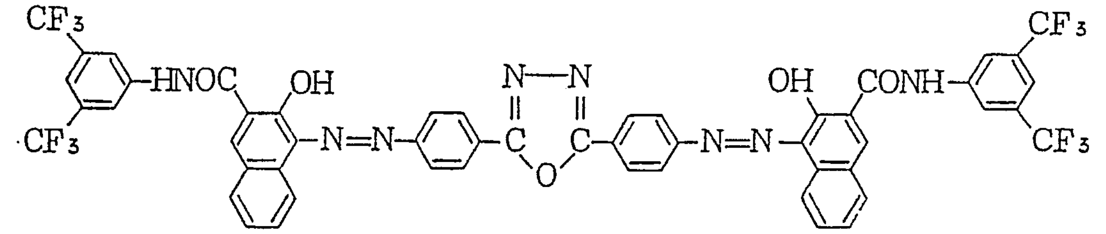

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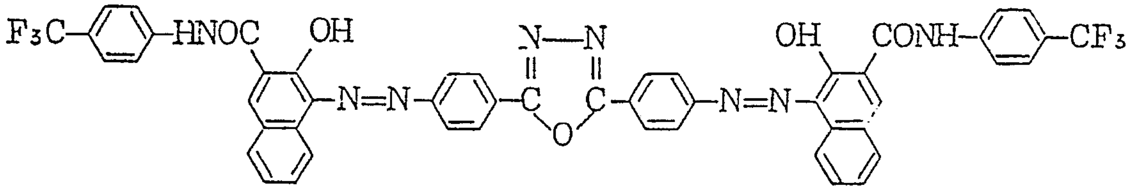

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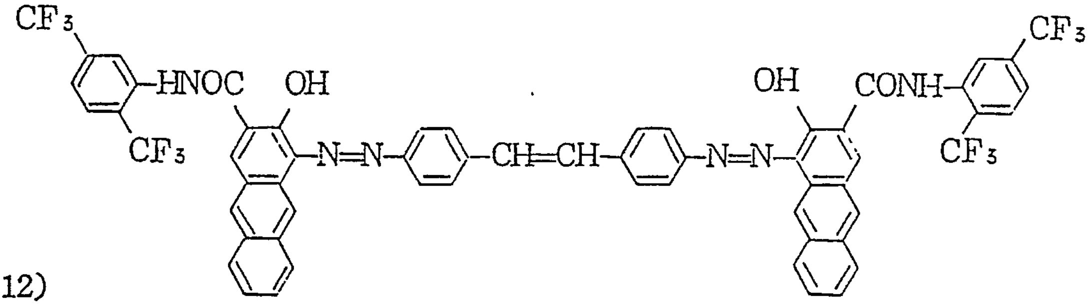

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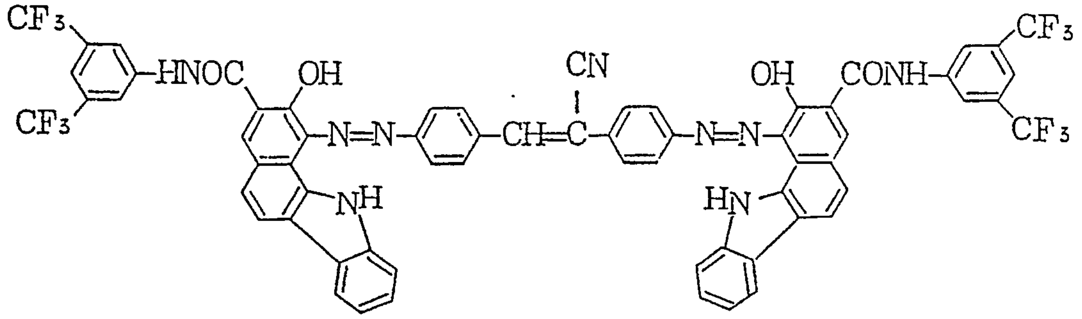

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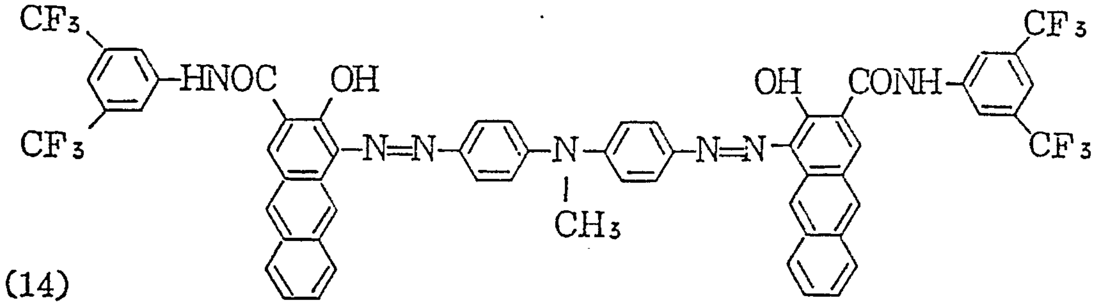

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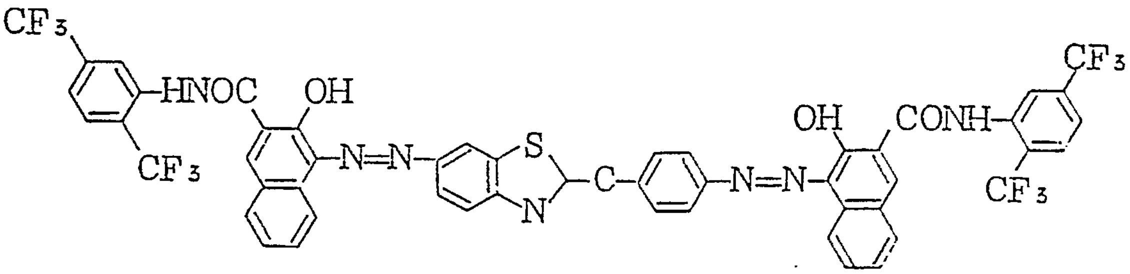

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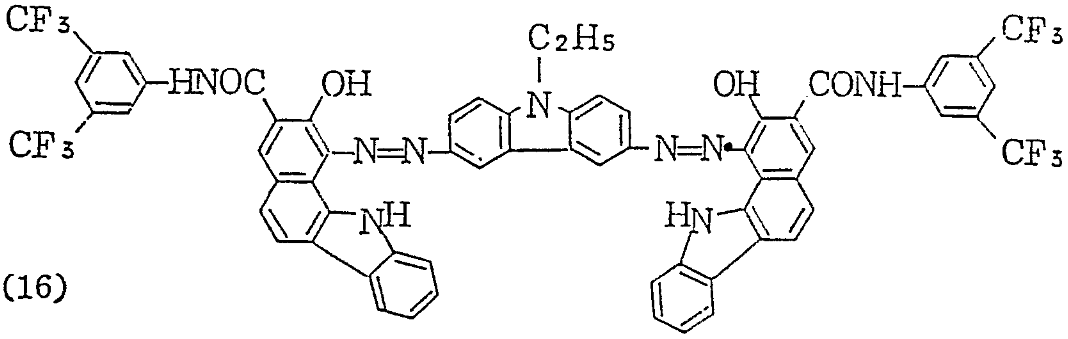

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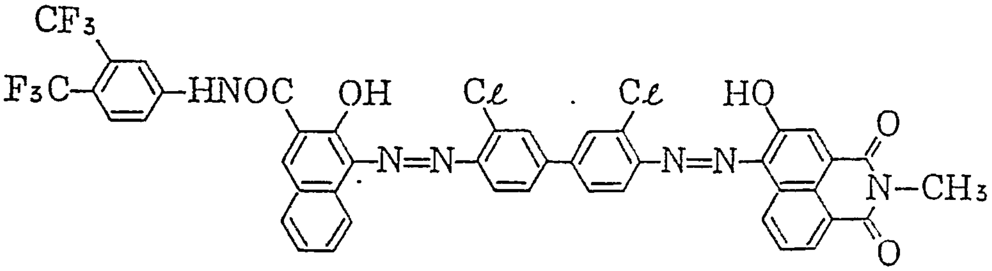

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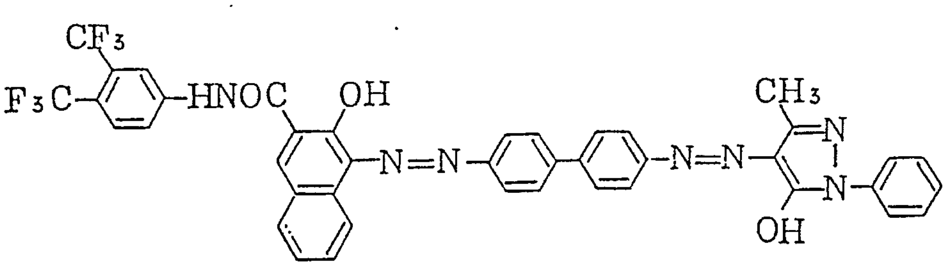

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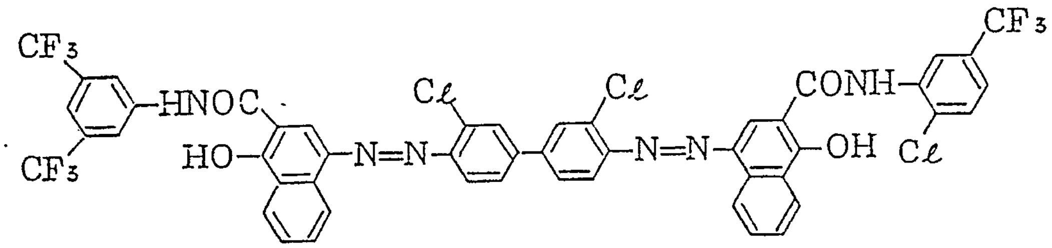

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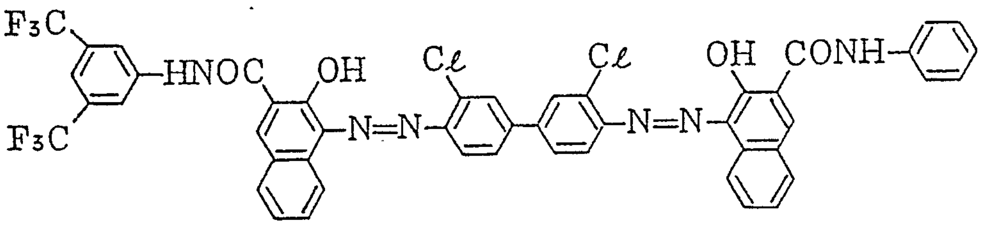

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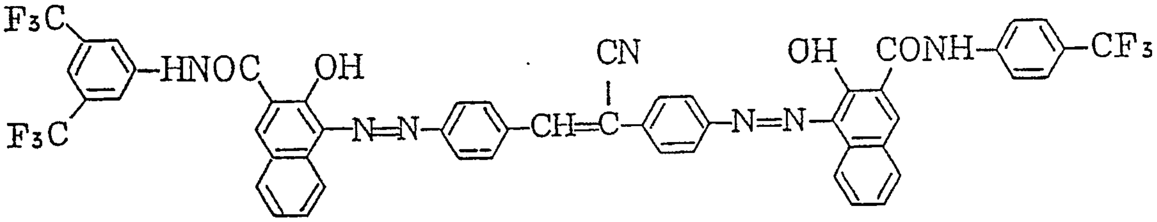


The above compounds can be synthesized by conventional methods. Synthesis of the compound where Cp_1 and Cp_2 are identical is shown below.

That is, it can be easily synthesized by tetrazotizing a diamine represented by the formula H_2N-A-NH_2 - (wherein A is as defined above) by conventional method and then coupling the tetrazonium salt with a corresponding coupler in the presence of an alkali or by once isolating the tetrazonium salt of the diamine as a borofluoride or a double salt with zinc chloride and then coupling it with a coupler in a solvent such as N,N-dimethylformamide or dimethylsulfoxide in the presence of an alkali.

Synthesis example of a typical example of the azo compound used in the present invention is shown below.

Synthesis Example (Compound No. 7 mentioned hereinbefore):

3.8 g (0.015 mol) of 3,3′-dichlorobenzidine was added to a mixed solution comprising 3.5 ml of concentrated hydrochloric acid, 20 ml of water and 20 ml of dimethylsulfoxide and dispersed therein. To the dispersion was added dropwise a solution prepared by dissolving 2.76 g (0.04 mol) of sodium nitrite in water under ice cooling and reaction was allowed to proceed for about 1 hour under cooling. Then, active carbon was added thereto, followed by filtration to obtain an aqueous solution of tetrazonium.

12 g (0.03 mol) of 2-hydroxy-3-α,α,α,α′,α′,α′-hexafluoro-3′,5′-xylyl)naphthoic acid amide (m.p. 235-236.5°C) as a coupling component and 15 g (0.1 mol) of triethanolamine as an organic amine were dissolved in 1000 ml of DMF and the solution was cooled to 0-5°C. Then, the above tetrazonium salt solution was added dropwise to the coupler solution and the resulting bluish purple pasty liquid was kept at 0-10°C and was further stirred for 3 hours. The resulting precipitate was filtrated and sufficiently washed with acetone and then with water and finally with again acetone and dried to obtain 8.9 g of blackish blue powder having a melting point of 350°C or higher.

The azo compounds used in the present invention where Cp_1 and Cp_2 are different are also synthesized by conventional method in two stages of coupling with the first coupling component and that with the second coupling component.

The azo compound of the above formula (I) shows substantially no photosensitivity when it is dispersed as it is in a polymer and a photoconductive layer is formed therefrom, but shows high photosensitivity when a carrier transport material referred to hereinafter is added thereto.

Content of the azo compound in photoconductive layer is not critical, but suitably is 30% by weight or less and preferably 5-30% by weight for obtaining good dissolving-away properties in practical use.

As organic solvents used for heating and stirring treatment in the present invention, mention may be made of, for example, ketone solvents such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, aromatic solvents such as toluene and xylene, ester solvents such as ethyl acetate and n-butyl acetate, halogenated hydrocarbon solvents such as chlorobenzene and dichloromethane, ether solvents such as tetrahydrofuran and dioxane, and dimethylformamide and dimethylacetamide. Especially preferred are ester solvents.

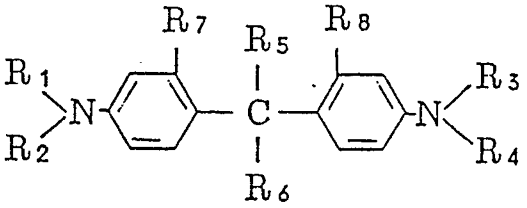
Conditions such as temperature and time for the heating and stirring treatment are determined considering characteristics as electrophotographic photoreceptor and dissolving-away properties of the photosensitive layer and preferably are 30-60 minutes at 40-80°C. When heat treatment for a long time at high temperature is conducted, sometimes electrophotographic characteristics or dissolving-away properties of photosensitive layer are adversely affected. After the heating and stirring treatment, the azo compound may be used at dry state by evaporation of solvent, but preferably is used at wet state.

The heat treatment of azo compound with organic solvent in the present invention means transformation of crystal of the azo compound, but does not merely mean enhancement of sensitivity of photosensitive layer, but also improves dissolving-away properties of photosensitive layer.

The third component in the present invention is the carrier transport material. When the azo compound alone is dispersed in a binder to form a photosensitive layer, such layer is very low in photosensitivity. Especially, in the use for lithographic printing plate made by dissolving and removing the photosensitive layer with a dissolution solution, amount of the carrier transport material insoluble in the dissolution solution including the azo compound should be as small as possible. Under such circumstances, a carrier transport material which is effective in a small amount is necessary.

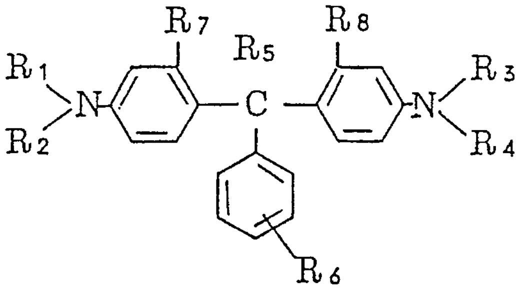
Various known carrier transport materials can be used in the present invention. However, in the use for printing plate, especially in the case of carrying out laser scanning exposure, a long time is required before toner development and thus dark decay of surface potential of the photosensitive layer is desired to be as small as possible. Normally, when photosensitivity is enhanced, dark decay is great. In order to reduce dark decay and simultaneously obtain high sensitivity, carrier transport materials of diarylalkanes and triphenylmethanes represented by the following formulas are preferred for the azo compounds used in the present invention.

Diarylalkanes:



(wherein R_1, R_2, R_3 and R_4 which may be identical or different each represents a hydrogen atom, a methyl group, an ethyl group, a benzyl group or a benzyl group having substituent, R_5 and R_6 which may be identical or different each represents a hydrogen atom or an alkyl group, and R_7 and R_8 which may be identical or different each represents a hydrogen atom, an alkyl group, an alkoxy group or a halogen atom).

Triphenylmethanes:

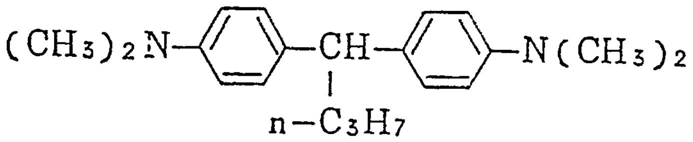


(wherein R_1, R_2, R_3 and R_4 which may be identical or different each represents a hydrogen atom, a methyl group, an ethyl group, a benzyl group or a benzyl group having substituent, R_5 represents a hydrogen atom or an alkyl group and R_6, R_7 and R_8 which may be identical or different each represents a hydrogen atom, an alkyl group, an alkoxy group or a halogen atom).

Nonlimiting examples of the carrier transport materials are enumerated below.

Diarylalkanes:

(1)



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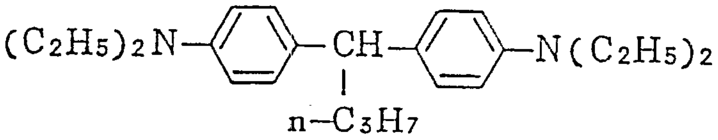

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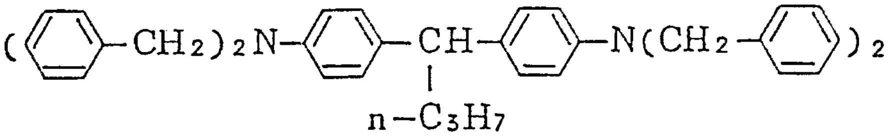

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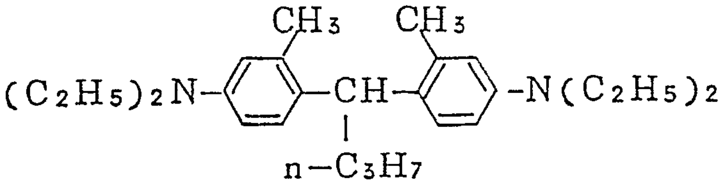

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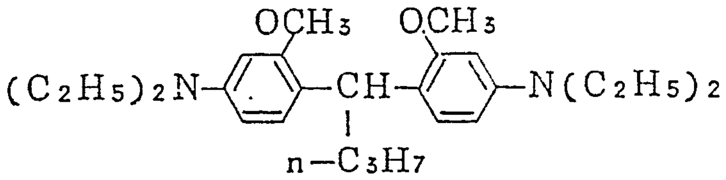

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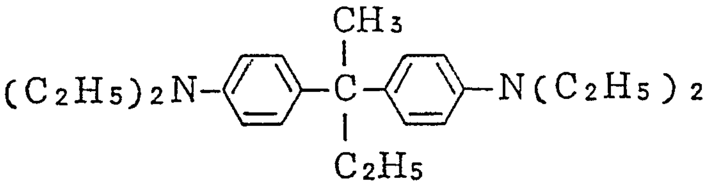

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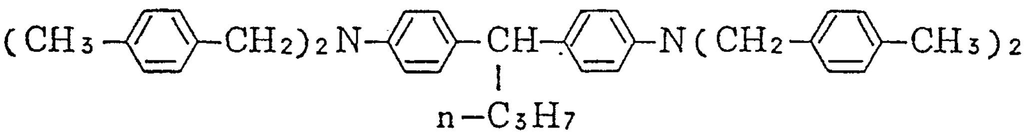

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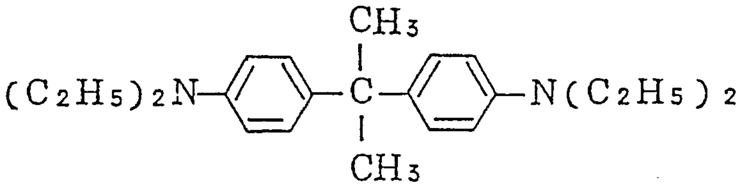

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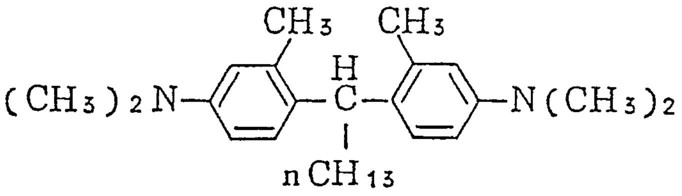

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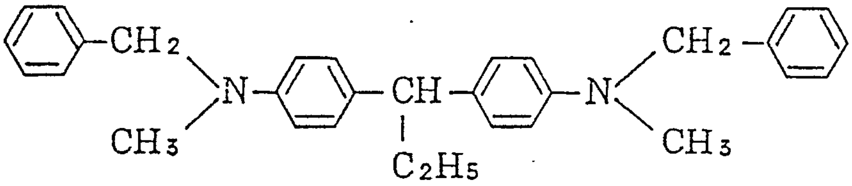

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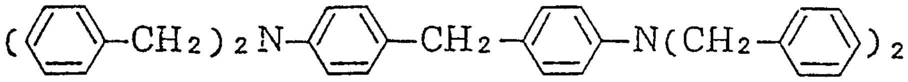

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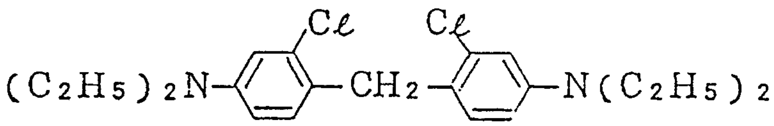
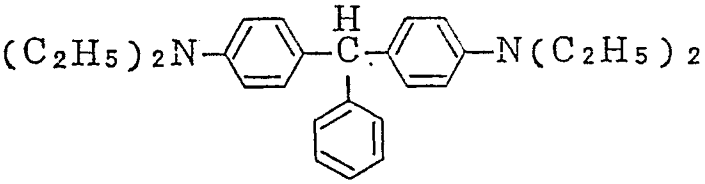


Triphenylmethanes:

(13)



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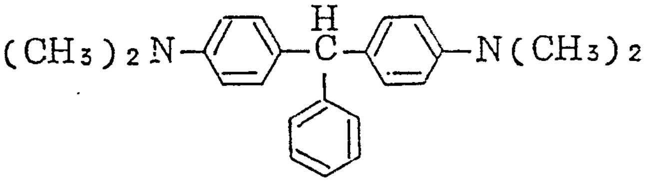

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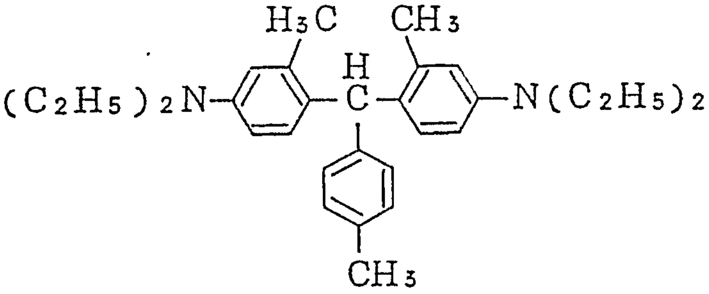

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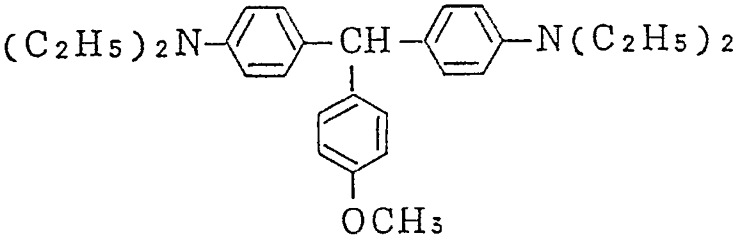

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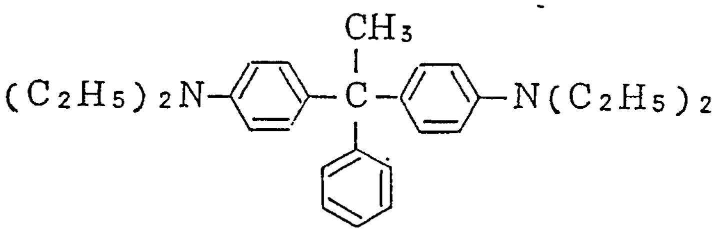

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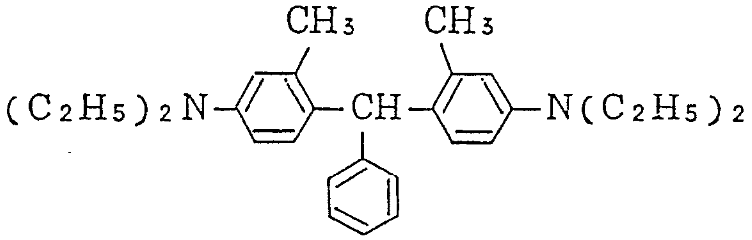
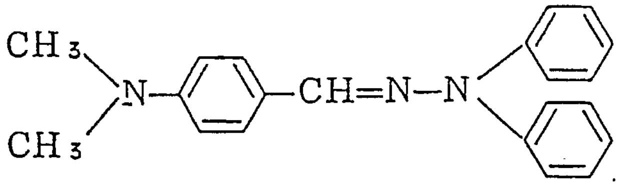


Hydrazones:

(19)



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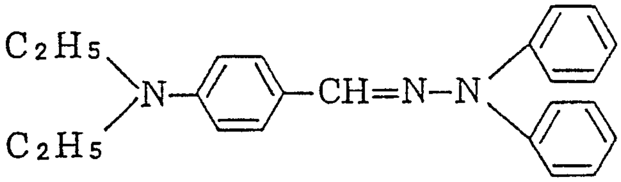

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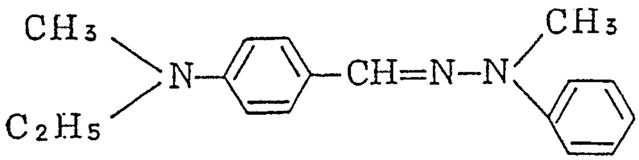

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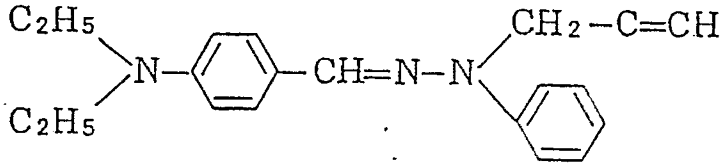

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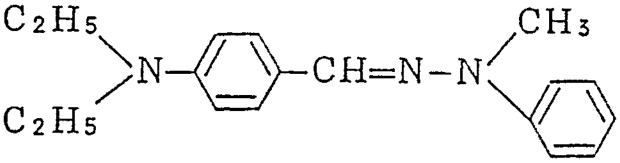

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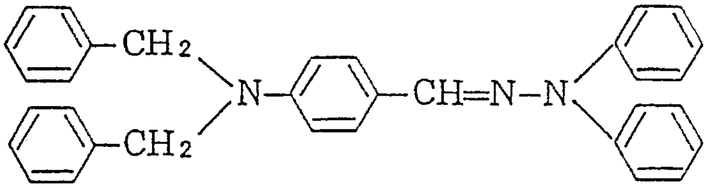

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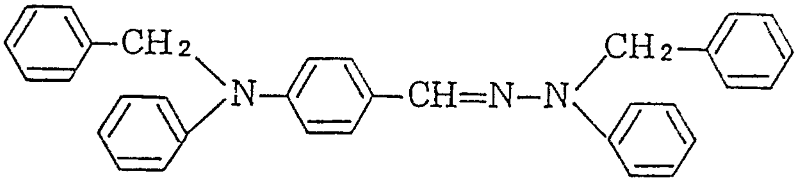

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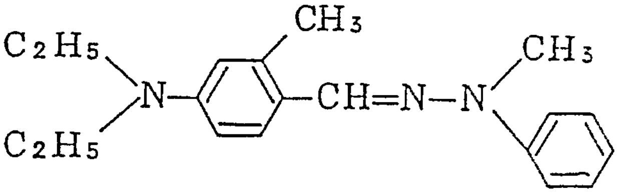

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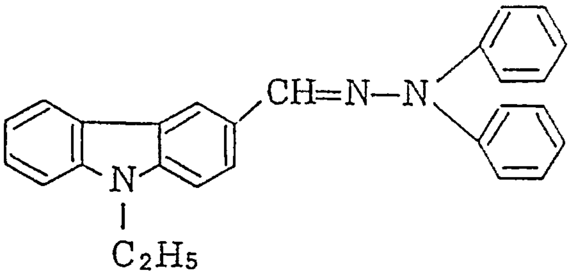

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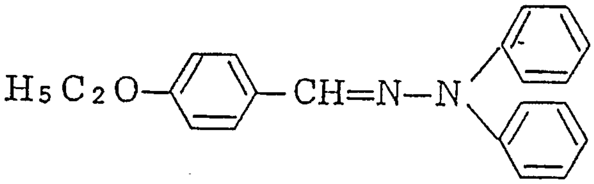

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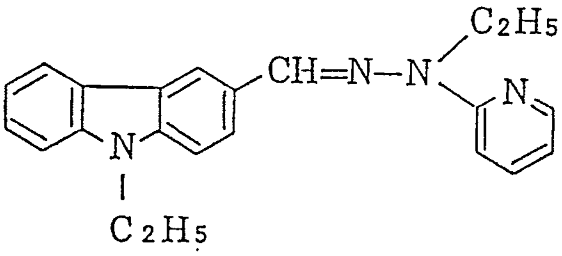

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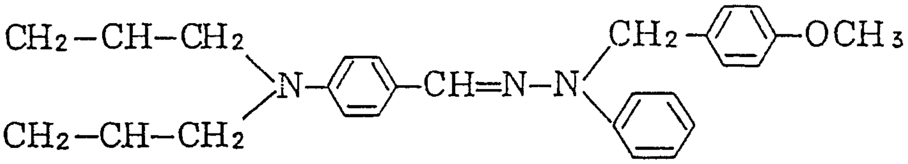

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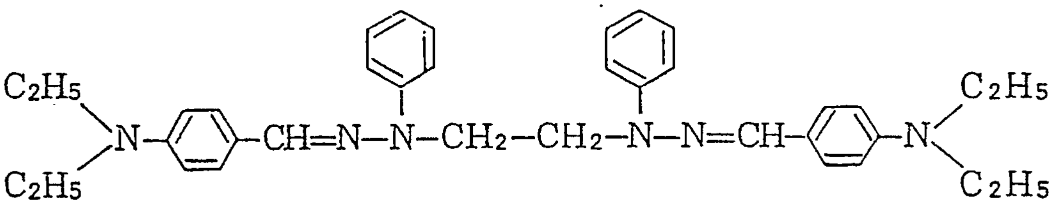

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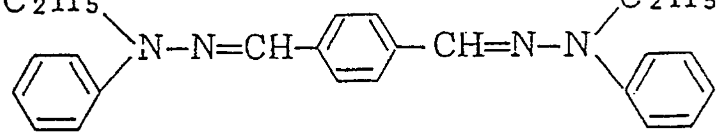

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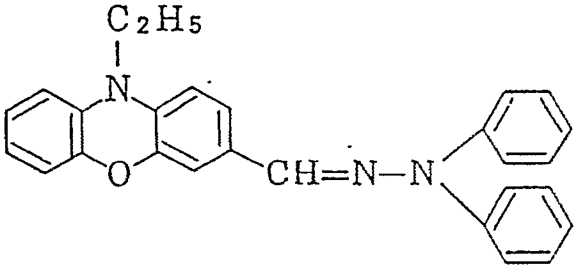

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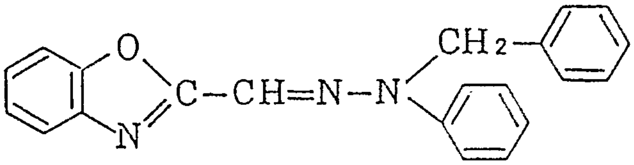

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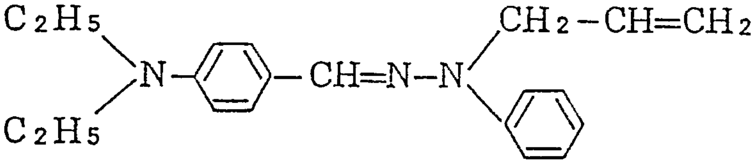

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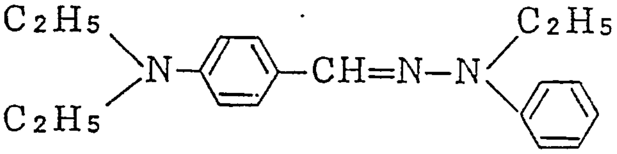

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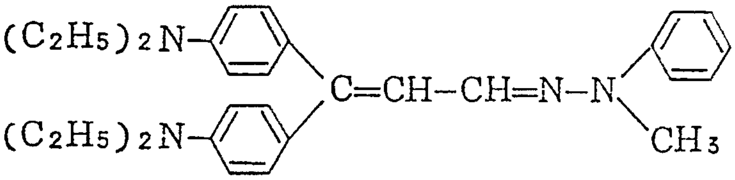

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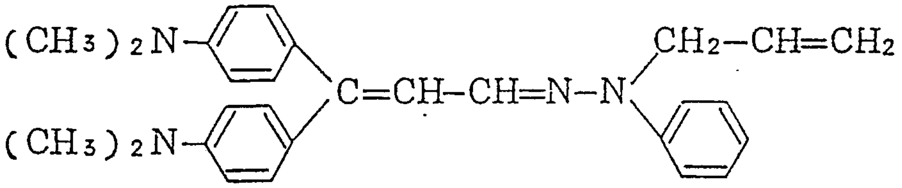
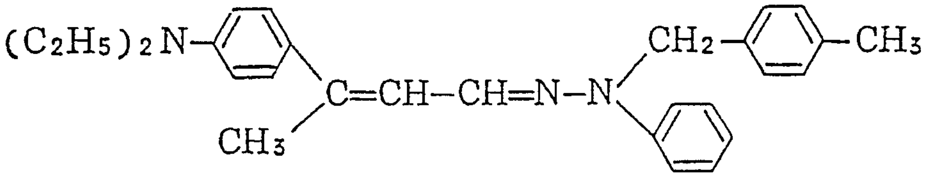
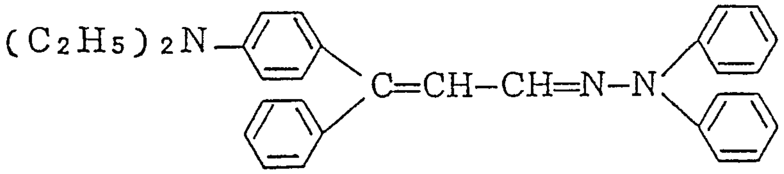

(CH3)2N
(CH3)2N
C=CH–CH=N–N
CH2–CH=CH2

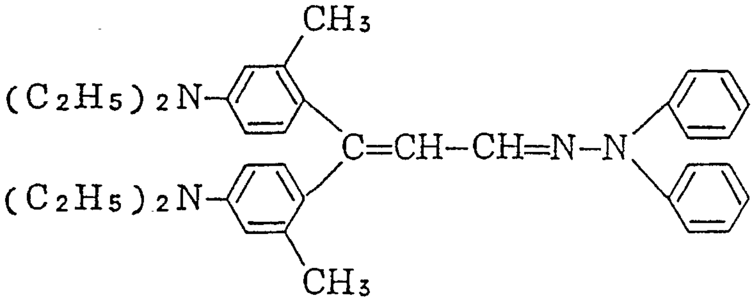
(39)


(C2H5)2N
C=CH–CH=N–N
CH3
CH2
CH3

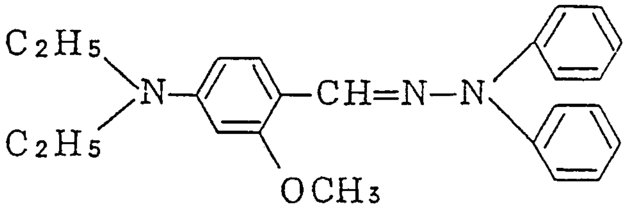
(40)


(C2H5)2N
C=CH–CH=N–N

(41)

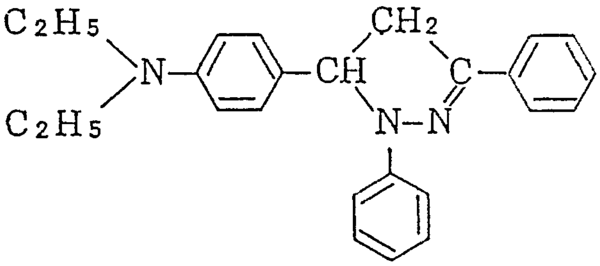

CH3
(C2H5)2N
(C2H5)2N
C=CH–CH=N–N
CH3

(42)


C2H5
C2H5
N
CH=N–N
OCH3

Pyrazolines:

(43)



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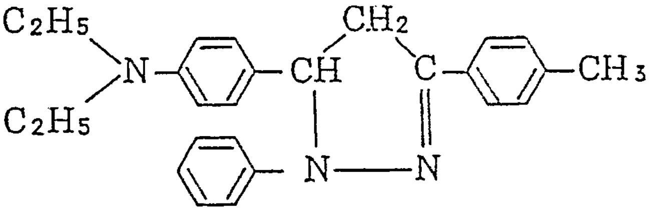

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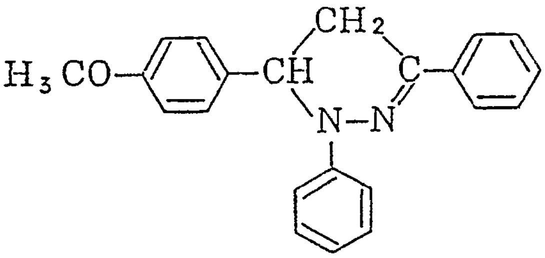

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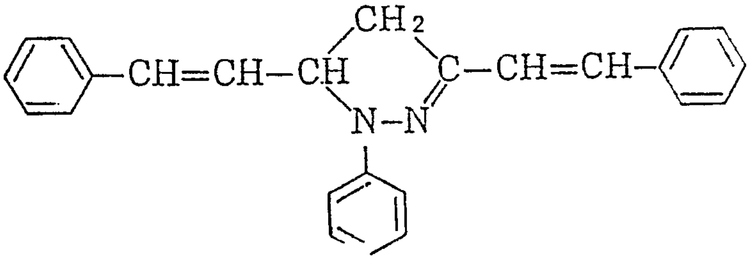

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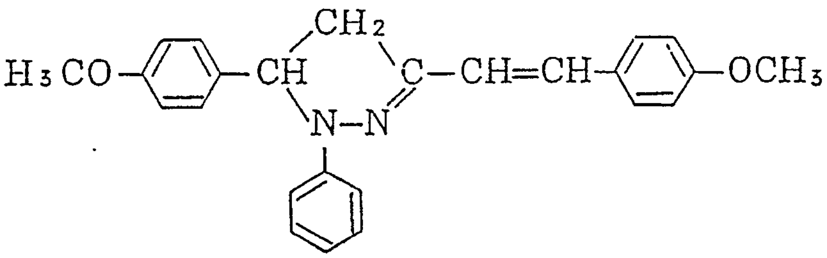

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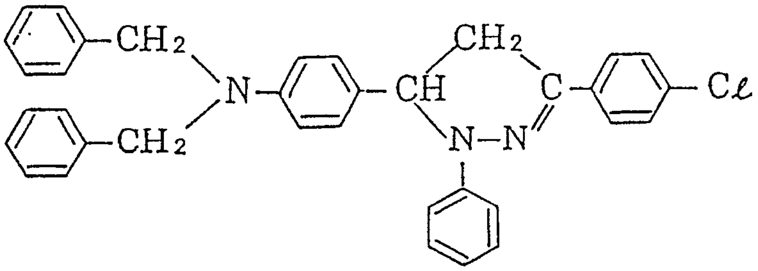

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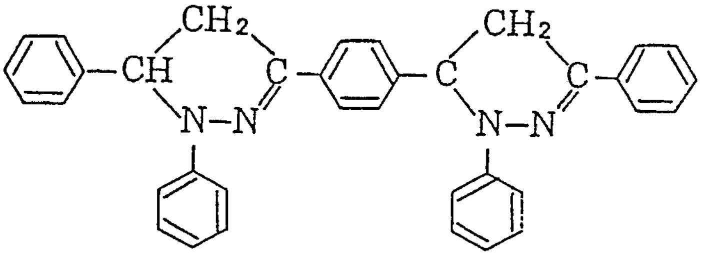

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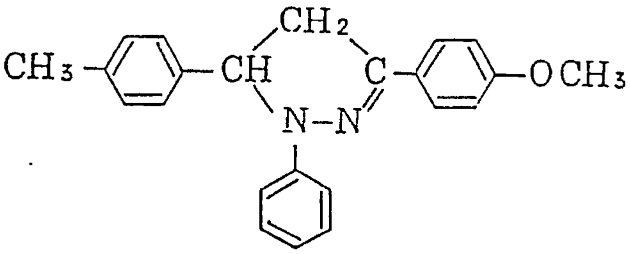

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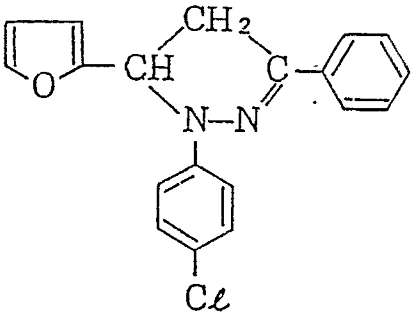

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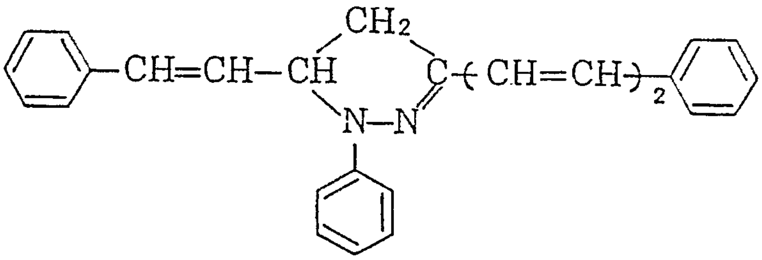

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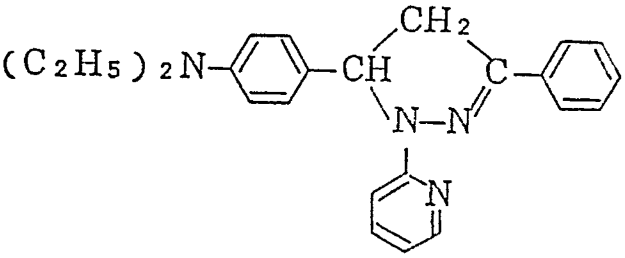

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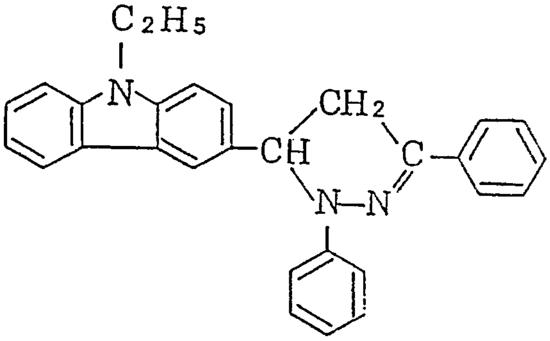

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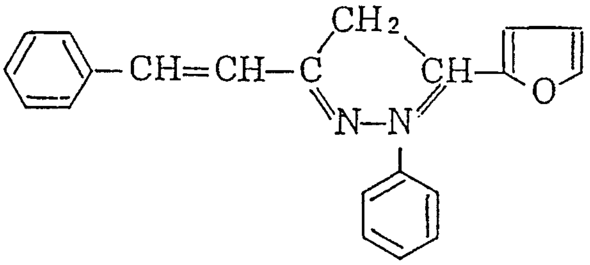

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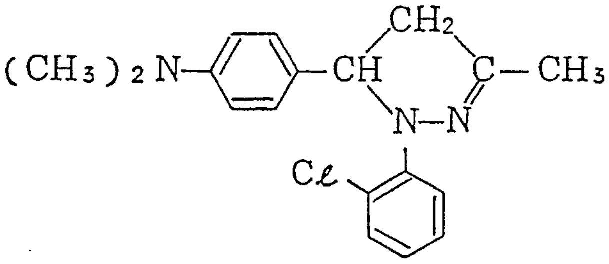

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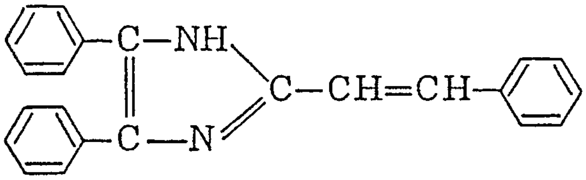

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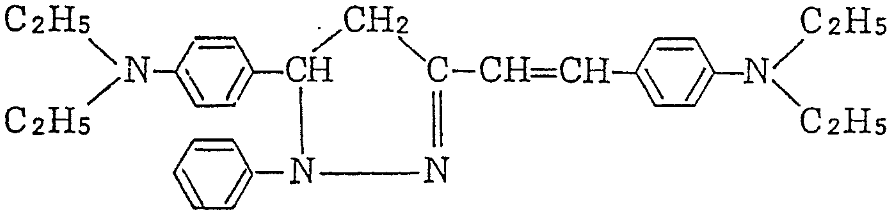

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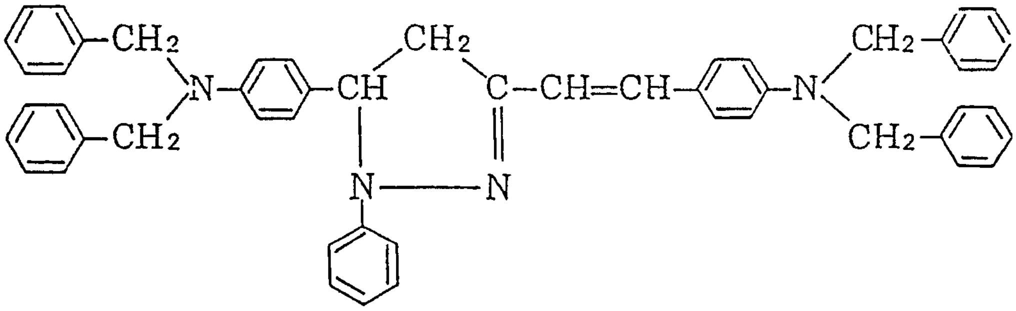
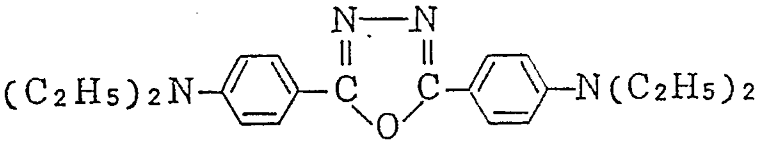


Oxadiazoles:

(60)



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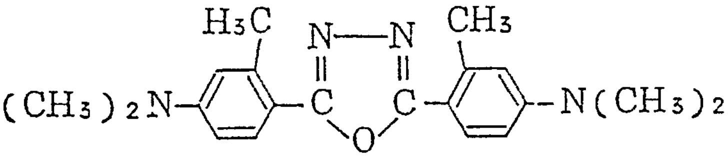

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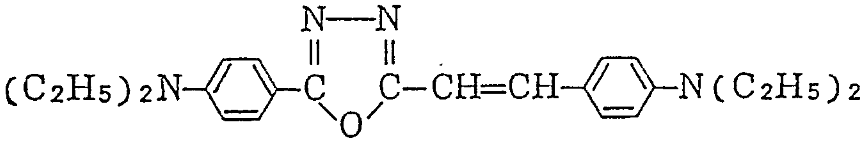

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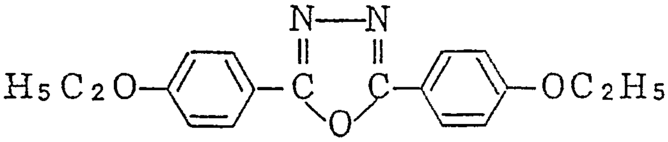

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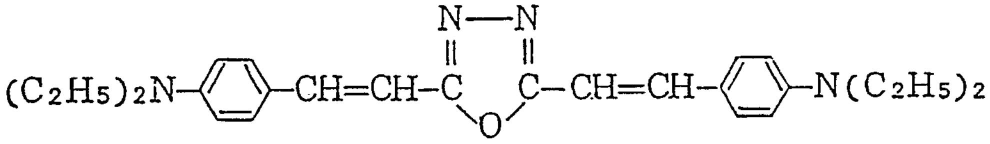

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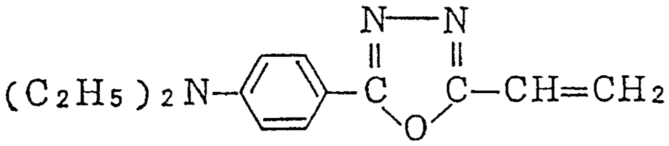


The above carrier transport materials normally act as hole transport materials and are added in a large amount in binder, but in the present invention, they exhibit the effect to increase photosensitivity in a smaller amount than the azo compound. It is assumed that in the present invention, the carrier transport material interacts on -CF_3 group on the surface of azo compound to reduce the surface barrier high to promote migration of photocarrier to outside and thus photosensitivity is enhanced.

Therefore, addition amount of the carrier transport material may be smaller than that of the azo compound in the preset invention. If it is added in a large amount, there occur problems such as reduction of charged potential and increase of dark decay. Therefore, it is preferred to use the carrier transport material in an amount of 5-80% by weight of the azo compound.

The printing plates according to the present invention is made by toner developing a printing plate material comprising an electrically conductive and hydrophilic base and, provided thereon, a photoconductive layer comprising the above-mentioned three components by electrophotographic process to form images, and washing away non-image portion other than the toner images by dissolving-out method.

As the base for printing plate materials of the present invention, there may be used all of the known bases of printing plate materials, for example, metal sheets such as aluminum sheet, zinc sheet, magnesium sheet and copper sheet; films and synthetic papers such as polyester, cellulose acetate, polystyrene, polycarbonate, polyamide and polypropylene; and coated papers such as resin-coated papers. However, since after formation of image, photoconductive compound and binder are removed by etching treatment and non-image portion must have hydrophilic property, bases having hydrophobic surface must be previously subjected to hydrophilic treatment. Metal sheets, especially aluminum sheets are most suitable and preferably they are subjected to surface treatments such as sand blasting treatment, alkali treatment, acid treatment and anodization treatment. In the case of films, it is preferred that they are coated with polymers of relatively high hydrophilicity, followed by crosslinking treatment or they are subjected to vapor deposition with a metal or laminated with a metal. When an insulating base is used, it is preferred to subject the surface of the base to electroconductive treatment.

The printing plate material of the present invention is made by adding the above three components to a solvent and dispersing them by a suitable known dispersing machine, for example, sand mill, colloid mill, homogenizer, and ultrasonic dispersing machine to prepare a coating liquid and coating this coating liquid at a thickness of 1-10 μ on the above support and drying the coat. The coating can be performed by known coating methods such as dip coating, bead coating, wire bar coating, blade coating, roller coating, curtain coating and extrusion coating.

The solvents usable here includes all organic solvents which can dissolve the binder and can dissolve or disperse the photoconductive compound.

As examples of these solvents, mention may be made of alcohols such as methanol, ethanol, propanol, butanol and hexyl alcohol, cellosolves such as methyl cellosolve, ethyl cellosolve and butyl cellosolve, aromatics such as benzene, toluene and xylene, cyclic ethers such as dioxane and tetrahydrofuran, esters such as ethyl acetate, butyl acetate and amyl acetate, ketones such as acetone, methyl isobutyl ketone and methyl ethyl ketone, dimethylformamide, dimethylsulfoxide and halogenated hydrocarbons. These may be used singly or in combination of two or more considering solubility, cost and safety.

The resulting printing plate material is subjected to image formation by electrophotographic process and non-image portion is dissolved away to make a printing plate.

Either of dry toner or wet toner may be used as toner for formation of image, but use of wet toner according to liquid developing is much preferred for obtaining print of excellent resolving power. Furthermore, for use as printing plate, the toner is required to be hydrophobic and ink-receptive and has adhesion high enough to stand printing and besides, to have resistivity against alkalis and alcohols when the non-image portion is dissolved away by alkali or alcohol. Toners which satisfy these requirements are dry toner comprising a mixture of iron powder with fine powder of a resin such as styrene resin, acrylic resin, polyester resin, epoxy resin or vinyl acetate resin and wet toner prepared by adding a charge control agent to a dispersion of the above resin in an electrically insulating isoparaffinic solvent or to a fine particle formed by polymerization of monomers of the above resin in an isoparaffinic solvent. The toner contains a pigment or dye for coloration in such amount as having no adverse effect on safety or fixability.

As dissolution solution for dissolving away the non-image portion, there may be used aqueous solutions of inorganic or organic various alkalis and/or alcohols. Inorganic alkalis include, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium phosphate, potassium phosphate, and ammonia and organic alkalis include, for example, amino alcohols such as monoethanolamine, diethanolamine and triethanolamine.

Alcohols include, for example, lower alcohols and aromatic alcohols such as methanol, ethanol, propanol and benzyl alcohol, and ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol and cellosolves.

Dissolvability of dissolution solution is selected depending on solubility of the photosensitive layer and degree of resistivity of the toner and designed considering dissolution rate, resolving power, image reproducibility and running processability. Generally, a small amount of surfactant is added to raise dissolution rate. After the non-image portion has been dissolved away, the plate can be subjected to washing with water, treatment with dilute aqueous acid solution or gumming treatment with aqueous solution of gum arabic to obtain advantageous effect to inhibit stain in background in printing or reproducibility of print image.

The following nonlimiting examples explain the present invention in more detail.

Example 1

20 g of chlorobenzene was added to 4.0 g of an azo compound [Compound (1) exemplified hereinbefore] and the mixture was stirred under heating at 70 °C for 1 hour. After the mixture was left to stand for cooling, to the mixture were added 1 g of a carrier transport material [Compound (3) exemplified hereinbefore], 20 g (solid content) of methacrylic acid-methacrylate ester copolymer (ester portion contained aliphatics such as propyl, butyl, hexyl, 2-ethylhexyl, and cyclohexyl) and 290 g of methyl cellosolve, followed by dispersing for 2 hours in a paint conditioner (manufactured by Red Davil Co.) together with 700 cc of glass beads to obtain a dispersion. This dispersion was coated on a sandblasted and anodized aluminum sheet and dried to make a printing plate material having a film of 5 µm thick.

Electrophotographic characteristics of this printing plate material were measured under the conditions of a corona voltage of -6.0 KV and tungsten lamp 10 lux using an electrostatic field measuring apparatus SP428 (manufactured by Kawaguchi Electric Co.).

Example 2

25 g of dimethylformamide was added to 5.0 g of an azo compound [Compound (16) exemplified hereinbefore] and the mixture was stirred under heating at 80 °C for 30 minutes. After the mixture was left to stand for cooling, thereto were added 1.0 g of a carrier transport material [Compound (60) exemplified hereinbefore], 18 g (solid content) of phenol resin, 90 g of dioxane and 200 g of methyl cellosolve. Thereafter, printing plate material was made and electrophotographic characteristics thereof were measured in the same manner as in Example 1.

Comparative Example 1

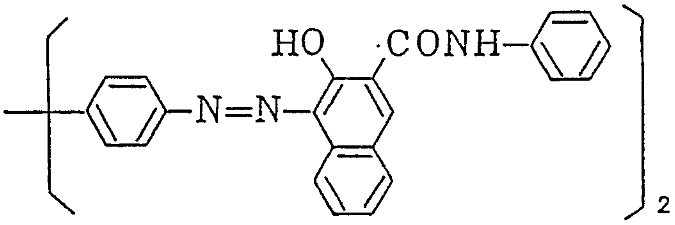
Printing plate material was made in the same manner as in Example 1 except that heat treatment of the azo compound was not carried out and electrophotographic characteristics were measured as in Example 1.

Comparative Example 2

Printing plate material was made in the same manner as in Example 1 except that methanol was used as the solvent for heat treatment and electrophotographic characteristics of the material were measured as in Example 1.

Comparative Example 3

Printing plate material was made in the same manner as in Example 2 except that the following comparative azo compound (A) was used as the azo compound and electrophotographic characteristics thereof were measured as in Example 1.



[A]

Comparative Example 4

Printing plate material was made in the same manner as in Comparative Example 3 except that heat treatment of the azo compound was not carried out and electrophotographic characteristics thereof were measured as in Example 1.

Electrophotographic characteristics of the printing plate materials made above are shown in Table 1.

Table 1

	Vo (initial potential: -V)	E1/2 (half decay exposure: lux sec)
Example 1	460	7.0
Comparative Example 1	470	22
Comparative Example 2	470	30
Example 2	450	6.8
Comparative Example 3	460	50
Comparative Example 4	460	60

As can be seen from Table 1, the printing plate materials of the preset invention had high sensitivity.

Next, the printing plate materials of the present invention (Examples 1 and 2) and those of Comparative Examples were set in commercially available plate making machine of electrophotographic type and were subjected to toner development and non-image portion was dissolved away with eightfold diluted solution of DP-4 (aqueous alkali solution manufactured by Fuji Photo Film Co., Ltd.), followed by water-washing and gumming to obtain lithographic printing plates.

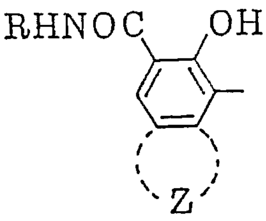
These printing plates were mounted on a forme rotary press OFFCON RR (manufactured by Ukita Kogyo K.K.) and printing was carried out. When the printing plates of the present invention were used, printing of 100,000 copies was carried out without staining of printed copies. The printing plates were examined to find no wearing-off of image and further printing was possible.

On the other hand, the printing plate materials of Comparative Examples 3 and 4 were low in sensitivity and much fogging occurred in the exposed portion and dissolution of non-image portion was inferior. In the case of the printing plate materials made in Comparative Examples 1 and 2, pigment remained after dissolving away of non-image portion to cause staining of printed copies. When the conditions for dissolving the non-image portion were strengthened so that pigment does not remained, line image became thin to cause defect of image.

From the above results, it can be seen that the printing plate materials of the present invention are high in sensitivity and are improved in dissolution of non-image portion and thus can provide electro photographic lithographic printing plates of high printing endurance and causing less stain of printed copies.

Claims

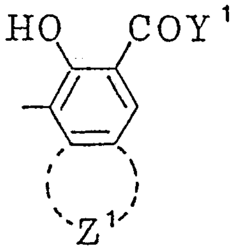
1. An electrophotographic lithographic printing plate material which comprises an electrically conductive and hydrophilic base and, provided thereon, a photoconductive layer, said photoconductive layer comprising:
a resin binder soluble in at least one member selected from the group consisting of an alkali and an alcohol,
an azo compound heat treated in an organic solvent excluding alcohol solvent and represented by the following formula (I):
$Cp_1 - N = N - A - N = N - Cp_2$ (I)
wherein A represents a divalent residue which bonds through its C atom to N atoms which constitute azo, Cp_1 and Cp_2 are identical or different and Cp_1 is a group represented by the formula:



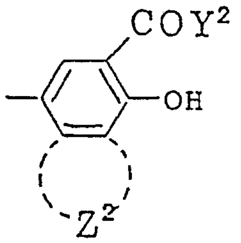
wherein Z represents a group of atoms necessary to form a substituted or unsubstituted carbocyclic aromatic ring, a substituted or unsubstituted heterocyclic aromatic ring or an unsaturated monocyclic hydrocarbon ring and R represents an aryl group having one or two CF_3 groups,and
a carrier transport material.

2. An electrophotographic lithographic printing plate material according to claim 1, wherein when Cp_2 is different from Cp_1, Cp_2 is a group represented by the following formula (a), (b), (c), (d), (e) or (f):

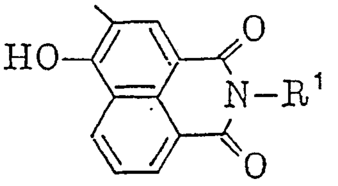
(a)



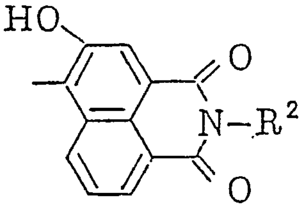
(b)



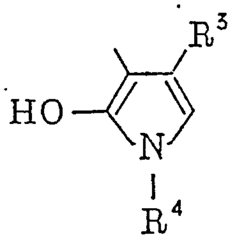
(c)



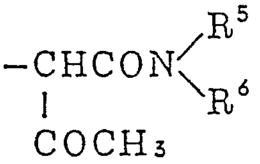
(d)



(e)



(f)



$-\underset{\displaystyle \mathrm{COCH_3}}{\mathrm{CH}}\mathrm{CON}\begin{smallmatrix} R^5 \\ R^6 \end{smallmatrix}$

wherein Z^1 and Z^2 each represents a group of atoms necessary to form a substituted or unsubstituted aromatic hydrocarbon ring or a substituted or unsubstituted heterocyclic ring, R^1 and R^2 each represents a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group, R^3 represents an alkyl group or a carboxyl group or an ester thereof, R^4 and R^6 each represents a substituted or unsubstituted aryl or heterocyclic group, R^5 represents a hydrogen atom or a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group, and Y^1 and Y^2 each represents $-NR^7R^8$, $-OR^9$, $-NHN=CH-R^{10}$ or $-NHNR^{11}R^{12}$ wherein R^7, R^8, R^9, R^{11} and R^{12} each represents a hydrogen atom or a substituted or unsubstituted alkyl, aralkyl, aryl or heterocyclic group and R^{10} represents a substituted or unsubstituted aryl or heterocyclic group,

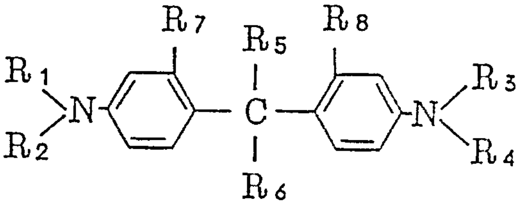
3. An electrophotographic lithographic printing plate material according to claim 1, wherein content of the azo compound in the photoconductive layer is 30% by weight or less.

4. An electrophotographic lithographic printing plate material according to claim 3, wherein content of the azo compound is 5-30% by weight.

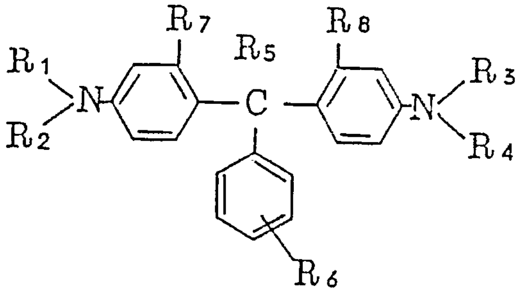
5. An electrophotographic lithographic printing plate material according to claim 1, wherein the heat treatment of the azo compound in the organic solvent is carried out at 40-80 °C for 30-60 minutes.

6. An electrophotographic lithographic printing plate material according to claim 1, wherein the organic solvent used for heat treatment of the azo compound is selected from the group consisting of a ketone solvent, an aromatic solvent, an ester solvent, a halogenated hydrocarbon solvent, an ether solvent, dimethylformamide and dimethylacetamide.

7. An electrophotographic lithographic printing plate material according to claim 1, wherein the carrier transport material is a diarylalkane or a triphenylmethane represented by the following formulas:
diarylalkane:



wherein R_1, R_2, R_3 and R_4 which may be identical or different each represents a hydrogen atom, a methyl group, an ethyl group, a benzyl group or a benzyl group having substituent, R_5 and R_6 which may be identical or different each represents a hydrogen atom or an alkyl group, and R_7 and R_8 which may be identical or different each represents a hydrogen atom, an alkyl group, an alkoxy group or a halogen atoms, triphenylmethane:



wherein R_1, R_2, R_3 and R_4 which may be identical or different each represents a hydrogen atom, a methyl group, an ethyl group, a benzyl group or a benzyl group having substituent, R_5 represents a hydrogen atom or an alkyl group and R_6, R_7 and R_8 which may be identical or different each represents a hydrogen atom, an alkyl group, an alkoxy group or a halogen atom.

8. An electrophotographic lithographic plate material according to claim 1, wherein content of the carrier transport material is 5-80% by weight of the azo compound.

9. An electrophotographic lithographic printing plate material according to claim 1, wherein the base is a metal sheet, a film, a synthetic paper or a coated paper.

10. A method for making an electrophotographic printing plate which comprises forming toner image on the electrophotographic printing plate material of claim 1 by electrophotographic process and then removing non-image portion other than the toner image by dissolving the portion with a solution mainly composed of at least one component selected from the group consisting of an alkali and an alcohol.