

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

Publication number:

**0 618 507 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21)

Application number: **94104886.0**

(51)

Int. Cl.<sup>5</sup>: **G03G 5/047, G03G 5/06**

(22)

Date of filing: **28.03.94**

(30)

Priority: **29.03.93 JP 70089/93**  
**14.04.93 JP 87380/93**

(43)

Date of publication of application:  
**05.10.94 Bulletin 94/40**

(84)

Designated Contracting States:  
**DE FR GB IT**

(71)

Applicant: **mitsubishi kasei corporation**  
**5-2, Marunouchi 2-chome**  
**Chiyoda-ku**  
**Tokyo 100 (JP)**

(72)

Inventor: **Nozomi, Mamoru**  
**A-301, 3, Sakuradai,**  
**Midori-ku**  
**Yokohama-shi, Kanagawa (JP)**  
Inventor: **Notsu, Shusuke**  
**28-6, Umegaoka,**  
**Midori-ku**  
**Yokohama-shi, Kanagawa (JP)**

(74)

Representative: **VOSSIUS & PARTNER**  
**Postfach 86 07 67**  
**D-81634 München (DE)**

(54)

**Electrophotographic photoreceptor for liquid development.**

(57)

An electrophotographic photoreceptor for liquid development comprising a conductive substrate having formed thereon at least a photoconductive layer containing a charge transporting material having a solubility in toluene of not more than about 13% by weight at 25 °C or a charge transporting material having a glass transition temperature of not lower than 50 °C.

**EP 0 618 507 A1**

This invention relates to an electrophotographic photoreceptor for liquid development and more particularly an electrophotographic photoreceptor for use in copying machines and photo printers utilizing liquid development for image formation.

Electrophotography has been steadily extending its application in the fields of not only copying machines but various printers because of rapid image formation and high image quality. As an electrophotographic photoreceptor (hereinafter simply referred to as a photoreceptor) which is a kernel of electrophotographic techniques, inorganic photoconductive materials, such as selenium, an arsenic-selenium alloy, cadmium sulfide, and zinc oxide, have conventionally been employed. In recent years, organic photoconductive materials have been developed owing to their advantages over inorganic ones, such as non-environmental pollution, ease of film formation, ease of production, and the like. Of the organic photoreceptors, so-called laminate type photoreceptors composed of a charge generating layer and a charge transporting layer have been chiefly studied.

Laminate type photoreceptors are composed of a charge generating material and a charge transporting material separately selected from the respective wide range so as to exhibit high efficiency, they have higher sensitivity and higher safety. Further, photoreceptors of this type are economically advantageous because of high productivity in coating operation. On account of these advantageous, laminate type photoreceptors have been extensively developed with expectation of taking the lead among various types of photoreceptors.

In the meantime, digitization in electrophotographic hardware, such as reading elements, writing elements, image processing devices, etc., has advanced rapidly with the aim of improving image quality in terms of resolving power, half tone reproducibility and the like. Along this line, it is well known that liquid development is a powerful means for accomplishing high image definition. As compared with dry development, liquid development uses much finer toner particles thereby realizing high resolving power and satisfactory image reproduction. A liquid developer to be used in liquid development generally comprises a highly insulating medium (solvent) having dispersed therein toner particles containing a dye or a pigment as a colorant and a binder resin and having added thereto a charge control agent to impart a prescribed charge quantity to the toner particles. However, a liquid development system is hardly utilized despite the superiority in achieving high definition but in limited fields, such as electrophotographic plate making and digital direct color proof (DDCP). In such fields, the development is carried out in a relatively large system so that countermeasures against dissipation of a solvent and recovery of a solvent are easily taken into hardware and the photoreceptor is rarely used repeatedly so that the problem of solvent resistance does not arise in practice. On the contrary, liquid development has not yet spread in the fields of copying machines and photo printers due to such obstructive problems as low safety of the solvent used, such as aliphatic hydrocarbons and fluorocarbons, environmental pollution by the dissipated solvent, and insufficient solvent resistance of the state-of-the-art photoreceptors.

While inorganic photoreceptors hold the lead for use in liquid development because of their durability against repeated use, it is desirable to use organic photoreceptors with the above-mentioned many advantages over inorganic ones.

Organic photoreceptors which have been so far proposed for use in liquid development include a photoreceptor comprising a mixed binder of an acrylic resin and a vinyl resin which are substantially insoluble in a paraffinic petroleum solvent (as described in JP-B-53-11856, the term "JP-B" as used herein means an "examined published Japanese patent application"), a photoreceptor having an overcoat layer comprising a resin insoluble in a liquid developer (as described in JP-A-52-89328, the "JP-A" as used herein means an "unexamined published Japanese patent application"), and a photoreceptor using a thermotropic liquid crystal resin. All these organic photoreceptors are of the type that is formed by using a binder resin and are aimed at prevention of deterioration of the binder resin due to softening, swelling, cracking, and the like on contact with a solvent of a liquid developer.

However, since photoreceptors of this type are generally produced by coating a substrate with a dispersion or a solution of a photosensitive composition, they essentially have poor solvent resistance. On examining solvent resistance of several commercially available organic photoreceptors, each of them proved insufficient in solvent resistance, suffering from corrosion with a solvent of a liquid developer.

The object of the present invention is to provide an electrophotographic photoreceptor for liquid development which has satisfactory resistance to a liquid developer even when immersed in or contacted with a liquid developer for a long period of time, suffers from no substantial deterioration in electrical characteristics even when used repeatedly, and always exhibits satisfactory characteristics as a photoreceptor.

The present inventors have ascertained that a charge transporting material, which is the main component of a photosensitive layer of an organic photoreceptor, is dissolved in a solvent of a liquid

developer, especially a trace amount of an aromatic hydrocarbon present as an impurity in the solvent to thereby cause deterioration of the photoreceptor characteristics.

The above object of the present invention is hence accomplished by using a specific charge transporting material having a low solubility in toluene, a representative of aromatic hydrocarbons, and found that the object is accomplished by using a charge transporting material having a glass transition temperature of not less than 50 °C.

Thus, the present invention relates to an electrophotographic photoreceptor for liquid development comprising a conductive substrate having thereon at least a photoconductive layer containing a charge transporting material, the charge transporting material having a solubility in toluene of not more than about 13% by weight at 25 °C. The term "solubility" as used herein means a weight percent of a charge transporting material as a solute in a saturated toluene solution.

The present invention also relates to an electrophotographic photoreceptor for liquid development comprising a conductive substrate having thereon at least a photoconductive layer containing a charge transporting material, the charge transporting material having a glass transition temperature (hereinafter referred to as T<sub>g</sub>) of not lower than 50 °C.

FIG. 1 is a powder X-ray diffraction pattern of the oxytitanium phthalocyanine pigment used in Examples 1 and 3.

In the present invention, a photoconductive layer is formed on a conductive substrate. Examples of the conductive substrate includes metallic substrates made of aluminum, stainless steel, copper, nickel, etc. and insulating substrates made of a polyester film, paper, etc. having provided thereon a conducting layer comprising aluminum, copper, palladium, tin oxide, indium oxide, etc. Preferred of them are aluminum or aluminum alloy substrates. Preferred species of aluminum materials include A1050, A3003, and A6063.

If desired, a known barrier layer may be provided between a conductive substrate and a photoconductive layer. The barrier layer may be an inorganic layer, such as anodized aluminum, aluminum oxide or aluminum hydroxide, or an organic layer, such as polyvinyl alcohol, casein, polyvinylpyrrolidone, polyacrylic acid, cellulose derivatives, gelatin, starch, polyurethane, polyimide, and polyamide.

In particular, an aluminum substrate having thereon an anodized aluminum film is preferred for satisfactory blocking effect. The aluminum substrate to be anodized is preferably degreased beforehand by washing with an alkali, an organic solvent, a surface active agent or an emulsion or by electrolysis. An anodized film is usually formed by anodizing in an acidic bath, such as chromic acid, sulfuric acid, oxalic acid, boric acid, sulfamic acid, etc. Anodizing in sulfuric acid is preferred since it gives the best results.

Anodizing in sulfuric acid is preferably carried out at a sulfuric acid concentration of from 100 to 300 g/l, a dissolved aluminum concentration of from 2 to 15 g/l, a liquid temperature of from 10 to 30 °C, an electrolytic voltage of from 5 to 20 V, and a current density of from 0.5 to 2 A/dm<sup>2</sup>. An anodized film is usually formed to a thickness of from 5 to 15 μm. If the film thickness is too small, the blocking effect tends to be small and fog tends to occur particularly in reversal liquid development. If it is too large, the cost incurred will be increased, and the anodized film tends to suffer from cracks, which will appear on images.

The thus formed anodized film is then subjected to a hole sealing treatment in which the film is immersed in an aqueous solution mainly containing nickel fluoride (low-temperature hole sealing treatment) or an aqueous solution mainly containing nickel acetate (high-temperature hole sealing treatment).

The low-temperature hole sealing treatment can be effected in the following manner: A nickel fluoride aqueous solution is most effectively used in a concentration of from 3 to 6 g/l, while not limiting. For satisfactory hole sealing treatment, it is preferably carried out at a temperature of from 25 to 50 °C, and more preferably from 30 to 35 °C, and the nickel fluoride aqueous solution preferably has a pH of from 4.5 to 6.5, and more preferably from 5.5 to 6.0. Examples of pH adjusting agents include oxalic acid, boric acid, formic acid, acetic acid, sodium hydroxide, sodium acetate, aqueous ammonia, and so forth. The treating time preferably ranges from 1 to 3 minutes per μm of the average film thickness. The nickel fluoride aqueous solution may contain cobalt acetate, nickel sulfate, a surface active agent, etc. for further improving properties of the film.

The high-temperature hole sealing treatment may be effected in the following manner: The hole sealing solution may be an aqueous solution of a metal salt, e.g., nickel acetate, cobalt acetate, lead acetate, nickel cobalt acetate or barium nitrate, with nickel acetate being preferred. In the case of a nickel acetate solution, its concentration is preferably from 3 to 20 g/l. The treatment is preferably carried out at a temperature of from 65 to 100 °C, and more preferably from 80 to 98 °C, and the nickel acetate aqueous solution preferably has a pH of 5.0 to 6.0. Examples of pH adjusting agents include aqueous ammonia and sodium acetate. The nickel acetate aqueous solution may contain sodium acetate, an organic carboxylic acid salt, an anionic or nonionic surface active agent, etc. for improving the properties of the film.

After the hole sealing treatment, it is preferable that the anodized film is thoroughly washed with water and dried. Since the surface of the anodized film is liable to be contaminated during anodizing, hole sealing, and washing, it is recommended to finally wash the surface by physical rubbing to clear the surface. The washing by rubbing is preferably conducted with a brush, a sponge or a cloth made of natural fibers, e.g.,  
 5 cotton, rayon, cellulose, and wool; synthetic fibers, e.g., polyester, nylon, acrylic fiber, and acetate fiber; foamed thermoplastics, e.g., polystyrene, polyethylene, and polypropylene; and foamed thermosetting plastics, e.g., polyurethane and polyurea.

The washing by rubbing can be performed by mechanically or manually giving a rotary motion and/or a reciprocating motion to the above-illustrated rubbing material in contact with the anodized film while  
 10 supplying a solvent, such as water, methanol or isopropyl alcohol therebetween.

The photoconductive layer used in the present invention may be a laminate type photoconductive layer composed of a charge generating layer and a charge transporting layer in this order or *vice versa*, a dispersion type photoconductive layer comprising a charge transporting medium having dispersed therein particles of a charge generating material.

In the case of the laminate type photoconductive layer, examples of charge generating materials to be used in the charge generating layer include inorganic photoconductive substances, e.g., selenium and its alloys, arsenic-selenium, cadmium sulfide, and zinc oxide; and various organic dyes or pigments, e.g., phthalocyanine pigments, azo dyestuffs, quinacridone pigments, polycyclic quinone pigments, pyrylium salts, thiapyrylium salts, indigoid dyes, thioindigoid dyes, anthanthrone dyes, pyranthrone dyes, and  
 20 cyanine dyes. Preferred of them are metal-free phthalocyanine; phthalocyanine compounds to which a metal, a metal oxide or a metal chloride, e.g., copper, indium chloride, gallium chloride, tin, oxytitanium, zinc, vanadium, etc., is coordinated; and azo pigments, e.g., monoazo pigments, bisazo pigments, triazo pigments, and polyazo pigments.

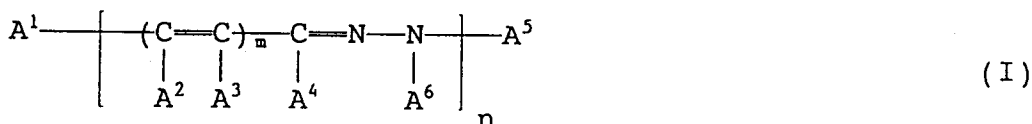
The charge generating layer may be prepared by dispersing fine particles of these charge generating materials in various binder resins, such as polyester resins, polyvinyl acetate, polyacrylic esters, polymethacrylic esters, polyesters, polycarbonates, polyvinyl acetoacetal, polyvinyl propional, polyvinyl butyral, phenoxy resins, epoxy resins, urethane resin, cellulose esters, and cellulose ethers. The charge generating material is used in an amount of from 30 to 500 parts by weight per 100 parts by weight of the binder resin. The charge generating layer usually has a thickness of from 0.1 to 2  $\mu\text{m}$ , and preferably from 0.15 to 0.8  
 30  $\mu\text{m}$ . If desired, the charge generating layer may contain various additives, such as leveling agents for improving coating properties, antioxidants, and sensitizers. The charge generating layer may be a deposited layer of the above-mentioned charge generating material.

The charge transporting layer basically comprises a charge transporting material and a binder resin.

According to the first embodiment of the present invention, a charge transporting material having a  
 35 solubility in toluene of not more than about 13% by weight, preferably from 1 to 13% by weight, and more preferably from 1 to 10% by weight, at 25 °C is used.

The solubility in toluene at 25 °C as referred to herein is a solubility as measured in the following manner: A charge transporting material is dissolved in toluene under heat to prepare a supersaturated solution, which is allowed to stand at 25 °C for 10 days with part of the charge transporting material precipitated. A given amount of the solution portion is distilled to remove toluene, and the residual charge  
 40 transporting material is weighed to obtain a weight ratio (%) to the solution, i.e., solubility in toluene at 25 °C.

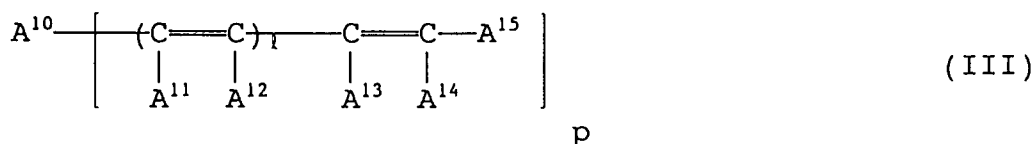
The charge transporting materials satisfying the above-mentioned solubility condition can be selected from known compounds. Examples thereof include compounds having a hydrazone structure, aromatic amine compounds, and the like compounds, such as compounds represented by formulae (I), (II) and (III) shown below, electron attracting substances, e.g., 2,4,7-trinitrofluorenone and tetracyanoquinodimethane; heterocyclic compounds, e.g., carbazole, indole, imidazole, oxazole, pyrazole, oxadiazole, pyrazoline, and thiadiazole; electron donating substances, e.g., aniline derivatives, hydrazone compounds, aromatic amine derivatives, and stilbene derivatives; and electron attracting or donating polymeric substances containing an  
 50 electron attracting or donating group of the above-enumerated compounds in the main chain or side chain thereof.



wherein A<sup>1</sup> represents a substituted or unsubstituted aromatic hydrocarbon residue or a substituted or unsubstituted aromatic heterocyclic residue, the substituent of which may contain a hetero atom; A<sup>2</sup>, A<sup>3</sup>, and A<sup>4</sup> each represent a hydrogen atom, a substituted or unsubstituted and saturated or unsaturated aliphatic hydrocarbon residue or a substituted or unsubstituted aromatic hydrocarbon residue; A<sup>5</sup> and A<sup>6</sup> each represent a substituted or unsubstituted and saturated or unsaturated aliphatic hydrocarbon residue, a substituted or unsubstituted aromatic hydrocarbon residue, or a substituted or unsubstituted aromatic heterocyclic residue; or A<sup>5</sup> and A<sup>6</sup> may be taken together to form a ring; m represents 0, 1, 2 or 3; and n represents 1 or 2.

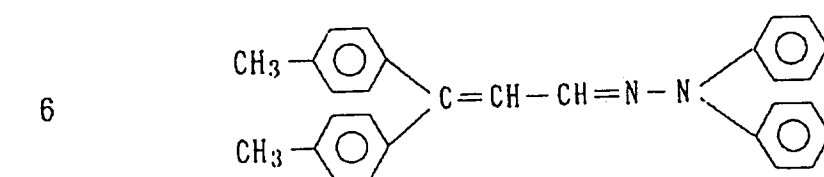
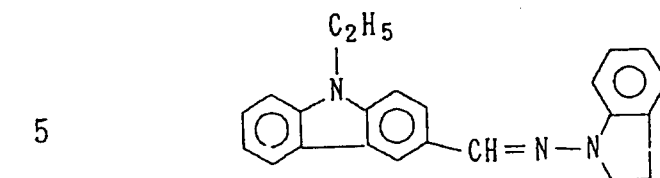
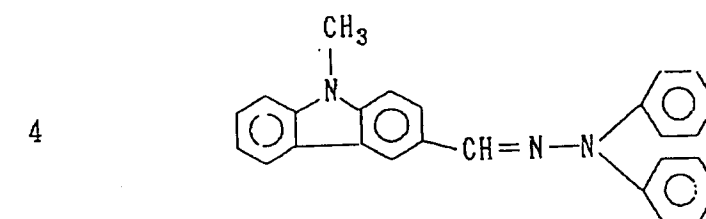
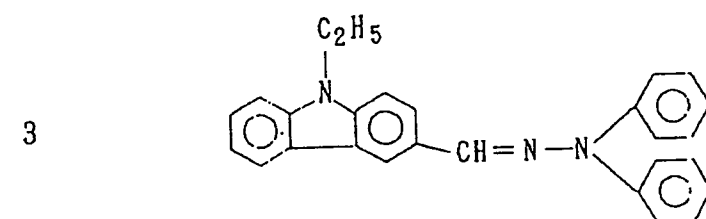
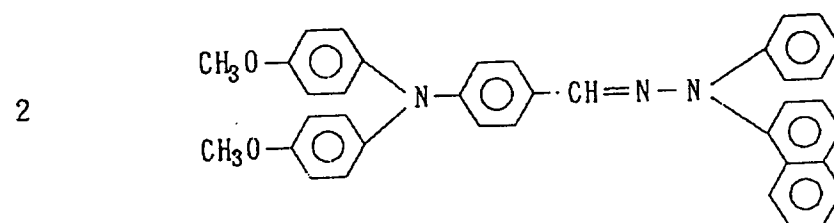
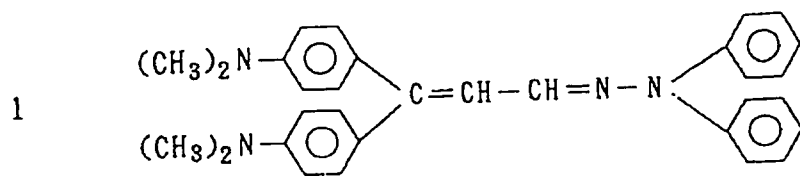


wherein A<sup>7</sup>, A<sup>8</sup>, and A<sup>9</sup> each represents a substituted or unsubstituted aromatic hydrocarbon residue or a substituted or unsubstituted aromatic heterocyclic residue, the substituent of which may contain a hetero atom; or A<sup>8</sup> and A<sup>9</sup> may be taken together to form a ring; and q represents 1 or 2.



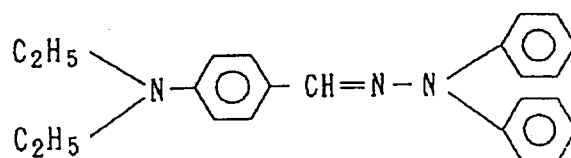
wherein A<sup>10</sup> represents a substituted or unsubstituted aromatic hydrocarbon residue or a substituted or unsubstituted aromatic heterocyclic residue, the substituent of which may contain a hetero atom; A<sup>11</sup>, A<sup>12</sup>, and A<sup>13</sup> each represent a hydrogen atom, a substituted or unsubstituted and saturated or unsaturated aliphatic hydrocarbon residue or a substituted or unsubstituted aromatic hydrocarbon residue; A<sup>14</sup> and A<sup>15</sup> each represent a substituted or unsubstituted and saturated or unsaturated aliphatic hydrocarbon residue, a substituted or unsubstituted aromatic hydrocarbon residue, or a substituted or unsubstituted aromatic heterocyclic residue; or A<sup>14</sup> and A<sup>15</sup> may be taken together to form a ring; l represents 0, 1, 2 or 3; and p represents 1 or 2.

Specific examples of the charge transporting materials represented by formulae (I) to (III) are shown below.

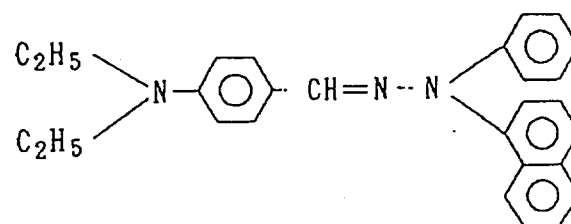


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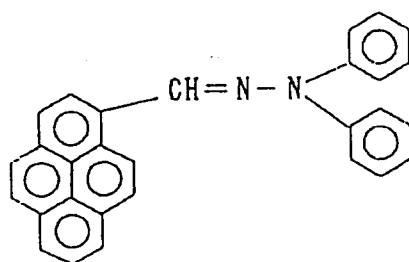
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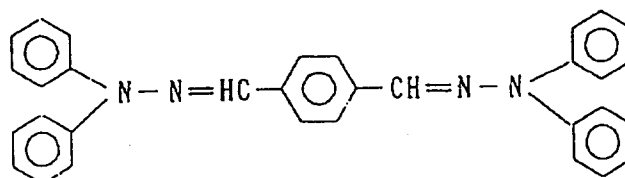
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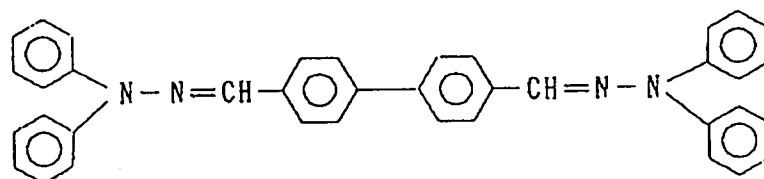


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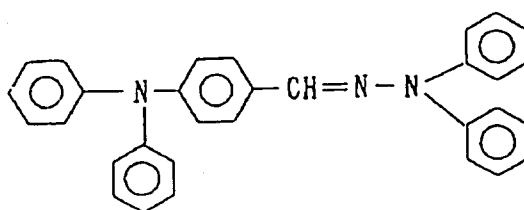
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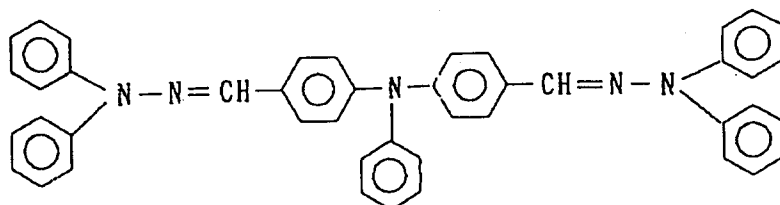
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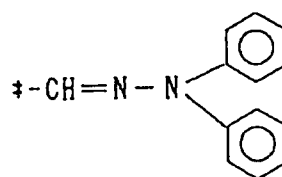
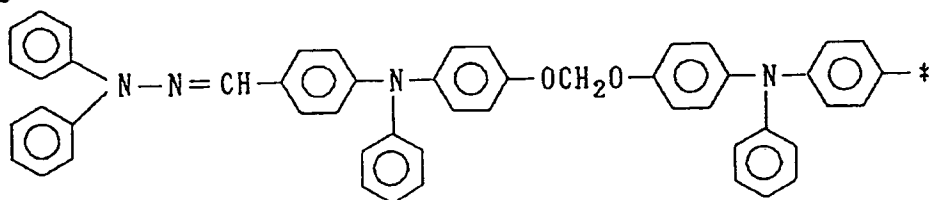
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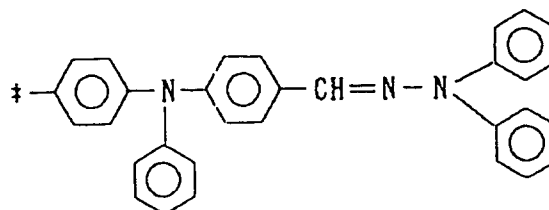
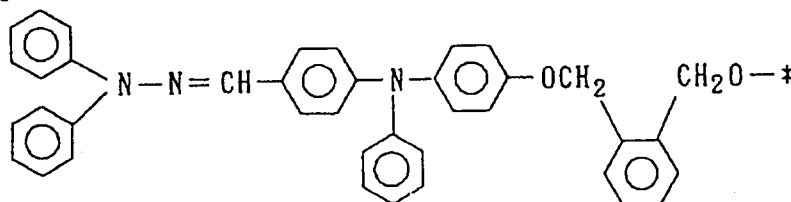
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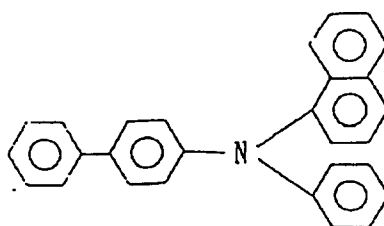


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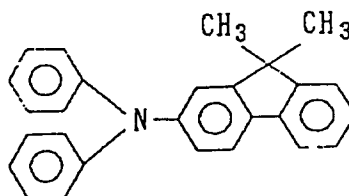




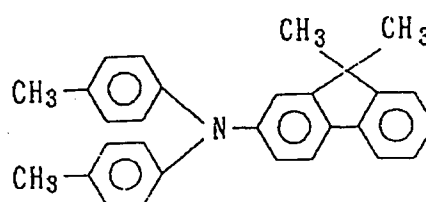
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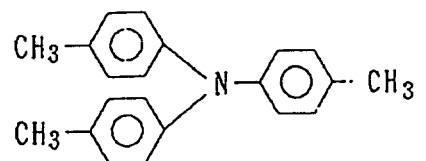
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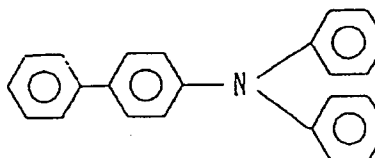
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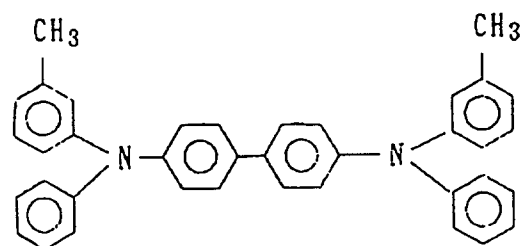
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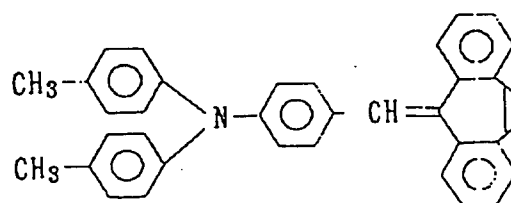
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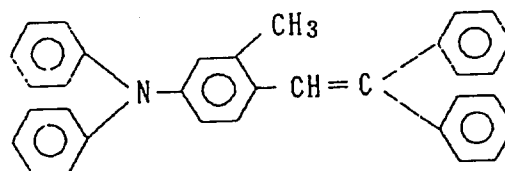
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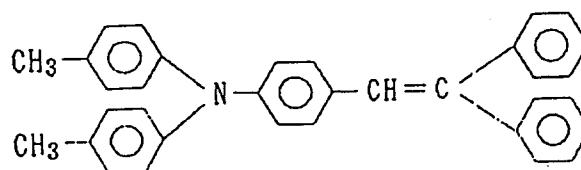
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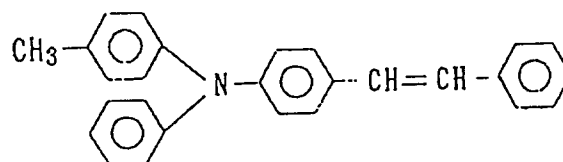
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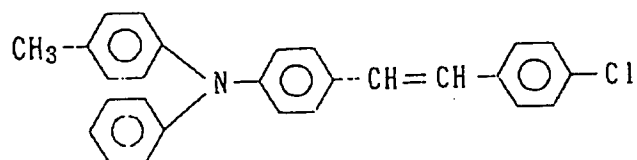
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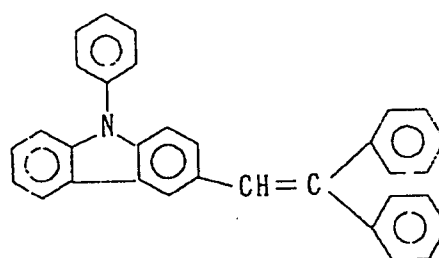
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thereof.

A charge transporting material having a very low solubility tends to meet difficulty in preparing a satisfactory coating solution, and that having a relatively high solubility has reduced solvent resistance. It is necessary therefore to select a charge transporting material so as to hold a good balance between coating properties and solvent resistance, taking the above tendencies into consideration.

According to a practice conventionally followed, an organic photoreceptor is mostly produced by coating, and the charge transporting material to be used has been required to have high solubility in a solvent for preparing a coating composition with satisfactory coating properties. To the contrary, the charge transporting material that can be used in the present invention preferably has low solubility in a solvent as having a solubility in toluene of not more than about 13% by weight, preferably from 1 to 13% by weight, and more preferably from 1 to 10% by weight, at 25 °C.

As previously described, charge transporting materials having a low solubility in toluene can be selected from the above-mentioned electron attracting or donating substances. In general, they are selected from materials having relatively satisfactory crystallizing properties, for example, those having a molecular structure of good symmetry, those having a stiff molecular structure, those having a polar group, and those having a high molecular weight.

In a second embodiment of the present invention, a charge transporting material having a Tg of not lower than 50 °C is used. Such a charge transporting material exhibits excellent resistance and stable characteristics as a photoreceptor.

The Tg of a charge transporting material as referred to herein is measured in the following manner: A powder of a charge transporting material is heated to melt and then rapidly cooled to prepare a glassy sample. The sample is heated in a differential scanning thermometer ("DSC-7000" manufactured by Shinku Riko Co., Ltd.) at a temperature increasing rate of 10 °C/min. The Tg is obtained from the resulting thermogram.

Charge transporting materials having a T<sub>g</sub> of not less than 50 °C can be selected from among the above-enumerated known charge transporting materials.

While it cannot be generally said what structure makes a charge transporting material have a Tg of not less than 50 °C, materials having relatively satisfactory crystallizing properties, for example, those having a molecular structure of good symmetry, those having a stiff molecular structure, those having a polar group, and those having a high molecular weight, tend to have a Tg of not less than 50 °C.

Examples of binder resins that can be used in the charge transporting layer include vinyl polymers, e.g., polymethyl methacrylate, polystyrene, and polyvinyl chloride, copolymers of the monomers constituting these vinyl polymers, polycarbonates, polyesters, polyester carbonates, polysulfone, polyimide, phenoxy resins, epoxy resins, and silicone resins. Partially crosslinked cured products of these resins may also be employed. The binder resins are essentially required to be substantially resistant to corrosion with a liquid developer and preferably substantially insoluble at least in toluene.

The charge transporting material is used in an amount usually of from 30 to 200 parts by weight, and preferably from 40 to 150 parts by weight, per 100 parts by weight of a binder resin.

If desired, the charge transporting layer may contain various additives, such as antioxidants and sensitizers.

The charge transporting layer generally has a thickness of from 10 to 60  $\mu\text{m}$ , preferably 19  $\mu\text{m}$  or more, and more preferably from 22 to 45  $\mu\text{m}$ . With a thickness of 19  $\mu\text{m}$  or more, and particularly from 22 to 45  $\mu\text{m}$ , a very satisfactory image can be obtained by liquid development probably for the following reason: With a surface potential of a photoreceptor being constant, as the thickness of a photosensitive layer increases, the field strength on the electrode surface is weakened so that injection of charges from the electrode seems to be lessened.

If desired, an overcoat layer mainly comprising a known material, such as a thermoplastic resin or a thermosetting resin, may be provided as the outermost layer. It is a practice generally followed to form a charge transporting layer on a charge generating layer, but the reversed order is also possible. Each layer can be formed by any known process, for example, by successive coating of a coating solution or dispersion of necessary components in a solvent.

In the case of a dispersion type photoconductive layer, a coating composition is prepared by dispersing the above-described charge generating material in a matrix comprising the above-described charge transporting material, binder resin and other additives at a ratio described above for the charge transporting layer. In this case, it is necessary that the charge generating material should have a sufficiently small particle diameter, generally not more than 1  $\mu\text{m}$ , and preferably not more than 0.5  $\mu\text{m}$ . If the amount of the charge generating material to be dispersed in a photosensitive layer is too small, sufficient sensitivity cannot be obtained. If it is too large, reductions in chargeability and sensitivity result. Accordingly, the charge generating material is generally used in an amount of from 0.5 to 50% by weight, and preferably from 1 to 20% by weight, based on the amount of the photoconductive layer.

The photosensitive layer generally has a thickness usually of from 5 to 50  $\mu\text{m}$ , preferably 19  $\mu\text{m}$  or more, and more preferably from 22 to 45  $\mu\text{m}$ . With a thickness of 19  $\mu\text{m}$  or more, and particularly from 22 to 45  $\mu\text{m}$ , a very satisfactory image can be obtained by liquid development.

If desired, the photosensitive layer may contain various known additives, such as plasticizers for improving film-forming properties, flexibility, mechanical strength, and the like, additives for controlling a residual potential, dispersants for improving dispersion stability, levelling agents for improving coating properties, surface active agents, silicone oils, fluorine oils, etc.

After coating a photoconductive layer and drying, the resulting organic photoconductive layer is preferably subjected to a heat treatment to obtain a satisfactory photoreceptor. While not limiting, the heat treatment is usually carried out at a temperature of 40 °C or higher, preferably 50 °C or higher, and more preferably 60 °C or higher, for a period of 30 minutes or longer, and preferably 60 minutes or longer. Heating at too high a temperature (e.g., 100 °C or higher) or for too long a period (e.g., 100 hours or longer), the photoreceptor is liable to be deteriorated. The heat treatment can be conducted in a usual manner, for example, by hot air heating in a chamber or a continuous hot air-circulating oven or by infrared or near infrared heating.

A liquid development system to which the photoreceptor of the present invention is applied is not particularly restricted, and examples thereof include a system using a liquid developer comprising the materials reported in Preprints of 25th Denshishashin Gakkai Koshukai (Preprints of 25th Lectures of Association of Electrophotography), p. 53 (1988). For instance, a liquid developer is prepared by dispersing a colorant, a resin and, if desired, a charge control agent in an insulating dispersion medium to prepare a stock toner having a concentration of from 5 to 30% and diluting the stock toner about 5 to 100 times with the dispersion medium. Examples of the dispersion media include organic solvents mainly comprising saturated hydrocarbons, e.g., Isopar G and H (produced by Exxon Chemical Co.), IP Solvent 1620 (produced by Idemitsu Petro-Chemical Co., Ltd.), Isododecane (isododecane, produced by BP Chemical Co.), and fluorocarbons.

The photoreceptor according to the present invention, which contains in its photoconductive layer a charge transporting material having a specific solubility in toluene or a specific Tg, exhibits satisfactory resistance to solvents of commonly employed liquid developers and undergoes no substantial deterioration in electrical characteristics even when used repeatedly. Not suffering from changes in appearance, such as cracks, dissolution and swelling, the photoreceptor provides satisfactory images with high definition. Thus having very high durability in liquid development, the photoreceptor of the present invention is broadly applicable to black-and-white or color copying machines and printers adopting liquid development.

The present invention will now be illustrated in greater detail with reference to Examples.

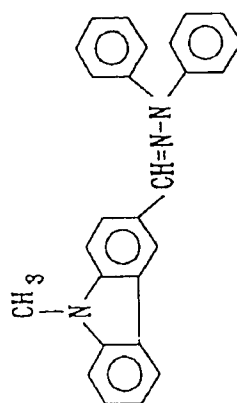
All the parts and percents are given by weight unless otherwise indicated.

Toluene solubility (at 25 °C) and Tg of the charge transporting materials used in Examples and Comparative Examples as measured in accordance with the above-described methods are shown in Table 1 below.

TABLE 1

Charge transporting material	Solubility in toluene at 25°C (wt%)	T <sub>g</sub> (°C)
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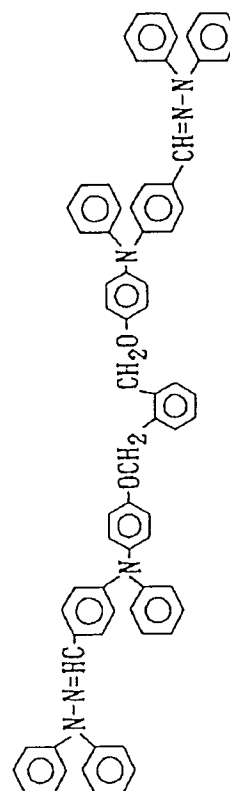
CTM-1



58

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CTM-2

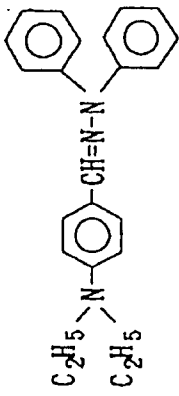
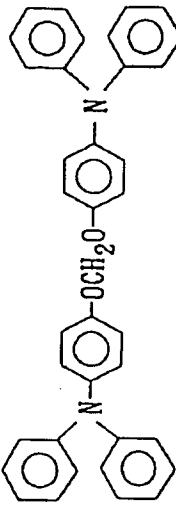


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9.5

(continued)

TABLE 1 (continued)

Tg (°C)	Solubility in toluene at 25°C (wt%)	Charge transporting material
18	60	<p data-bbox="634 1487 667 1576"><u>CTM-3</u></p> 
46	14	<p data-bbox="1014 1487 1047 1576"><u>CTM-4</u></p> 

## EXAMPLE 1

10 parts of oxytitanium phthalocyanine were added to 140 parts of 1,2-dimethoxyethane, and the mixture was finely dispersed in a sand mill to prepare a pigment dispersion. The oxytitanium phthalocyanine had powder X-ray diffraction pattern to CuX characteristic X-ray shown in Fig. 1. The pigment dispersion was added to a mixture of 100 parts of a 5% dimethoxyethane solution of polyvinyl butyral ("#6000-C" produced by Denki Kagaku Co., Ltd.) and 100 parts of a 5% dimethoxyethane solution of a phenoxy resin ("PKHH" produced by Union Carbide Co.) to prepare a dispersion having a solid content of 4.0%.

A polyethylene terephthalate film having deposited thereon a 1,000 Å thick aluminum layer was coated with the above-prepared dispersion by means of a wire bar to form a charge generating layer having a dry

thickness of 0.4 g/m<sup>2</sup>.

A solution prepared by dissolving 70 parts of CTM-1 shown in Table 1, 100 parts of a bisphenol A polycarbonate resin ("Novarex 7030A" produced by Mitsubishi Kasei Corp.), and 1.5 parts of 4-(2,2-dicyanovinyl)phenyl-2,4,5-trichlorobenzenesulfonate in a mixed solvent of 1,4-dioxane and tetrahydrofuran was applied to the charge generating layer with an applicator and dried at room temperature for 10 minutes and then at 125 °C for 15 minutes to form a charge transporting layer having a dry thickness of 17 μm.

The resulting photoreceptor was designated photoreceptor A.

## EXAMPLE 2

Photoreceptor B was prepared in the same manner as in Example 1, except for replacing CTM-1 with 60 parts of CTM-2 shown in Table 1.

## COMPARATIVE EXAMPLE 1

Photoreceptor C was prepared in the same manner as in Example 1, except for replacing CTM-1 with the same amount of CTM-3 shown in Table 1.

## COMPARATIVE EXAMPLE 2

Photoreceptor D was prepared in the same manner as in Example 1, except for replacing CTM-1 with the same amount of CTM-4 shown in Table 1.

Each of photoreceptors A to D was fitted to an electrostatic paper analyzer ("EPA-8100" manufactured by Kawaguchi Denki K.K.). After being charged to have a current of 35 μA flowing to the aluminum surface, the photoreceptor was exposed to light and destaticized. The initial potential (V<sub>0</sub>), a dark decay after 2 seconds from the charging (DD), a sensitivity (an exposure amount required for reducing the initial potential to half) (E<sub>1/2</sub>; lux·sec; reference potential: 500 V), and a residual potential (V<sub>r</sub>) were measured. The results obtained are shown in Table 2 below.

In order to evaluate solvent resistance of the photoreceptor, the photoreceptor was immersed in a commercially available solvent generally employed as a dispersion medium of a liquid developer ("Isopar L" produced by Esso Sekiyu K.K.; composed of 99.9% of saturated aliphatic hydrocarbons and, as impurities, 0.1% of aromatic hydrocarbons) at room temperature for 3 weeks and taken out. After 30 minutes, the electrophotographic properties were examined in the same manner as described above. The results obtained are shown in the parentheses in Table 2.

TABLE 2

Photoreceptor	V <sub>0</sub> (V)	DD (V)	E <sub>1/2</sub> (lux·sec)	V <sub>r</sub> (V)	Remark
A	691 (764)	29 (39)	0.30 (0.27)	14 (11)	Invention
B	578 (603)	37 (39)	0.38 (0.36)	8 (16)	"
C	550 (625)	45 (60)	0.35 (6.80)	7 (254)	Comparison
D	671 (723)	28 (37)	0.49 (5.30)	45 (235)	"

As is apparent from the results in Table 2, photoreceptors C and D containing a charge transporting material having a high toluene solubility and a T<sub>g</sub> of less than 50 °C undergo considerable changes in electrophotographic characteristics due to solvent immersion whereas no substantial changes were observed with photoreceptors A and B containing a charge transporting material having a low toluene solubility and a T<sub>g</sub> of not less than 50 °C, demonstrating stable electrophotographic characteristics. On examining the appearance of each photoreceptor after 3-week immersion in Isopar solvent, no change was observed with photoreceptors A and B, while photoreceptor C had a disturbed surface with a flow pattern. The surface of photoreceptor D was less disturbed than that of photoreceptor C, and yet showed a flow pattern.

## EXAMPLE 3

An aluminum cylinder having a thickness of 1 mm with its surface mirror-finished was degreased in a 30 g/l aqueous solution of a degreasing agent ("NG-#30" produced by Kizai K.K.) at 60 °C for 5 minutes. After washing with water, the cylinder was soaked in 7% nitric acid at 25 °C for 1 minute. After washing with

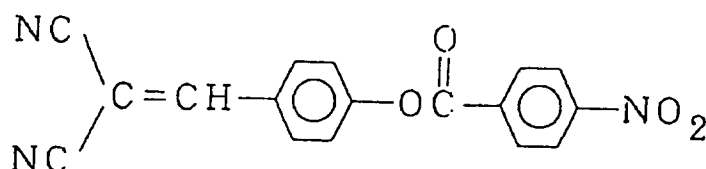
water, the cylinder was subjected to anodizing in a 180 g/l sulfuric acid electrolytic solution (dissolved aluminum concentration: 7 g/l) at a current of 1.2 A/dm<sup>2</sup> to form an anodized film having an average thickness of 8 μm. After washing with water, the cylinder was dipped in a 10 g/l aqueous solution of a high-temperature hole-sealing agent mainly comprising nickel acetate ("Topseal DX-500" produced by Okuno Seiyaku Kogyo K.K.) at 95°C for 30 minutes, followed by washing with water. Finally, the entire surface of the anodized film was cleaned by giving three reciprocal rubs with a polyester sponge, washed with water, and dried.

A mixture of 10 parts of oxytitanium phthalocyanine whose powder X-ray diffraction pattern to CuX characteristic X-ray is shown in FIG. 1, 5 parts of polyvinyl butyral ("S-Lec BH-3" produced by Sekisui Chemical Co., Ltd.), and 500 parts of 1,2-dimethoxyethane was finely dispersed in a sand mill to prepare a pigment dispersion. The pigment dispersion was applied to the above-prepared aluminum substrate having an anodized film by dip coating to form a charge generating layer having a dry thickness of 0.4 g/m<sup>2</sup>.

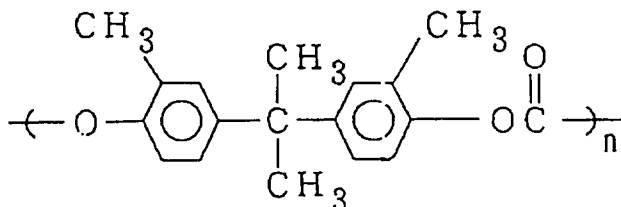
A solution prepared by dissolving 60 parts of CTM-2 shown in Table 1, 1.5 parts of a cyano compound having the formula shown below, and 100 parts of a polycarbonate resin having the formula shown below (viscosity-average molecular weight: 30,000) in 1,000 parts of 1,4-dioxane was applied to the charge generating layer by dip coating to form a charge transporting layer having a dry thickness of 20 μm.

The resulting photoreceptor was designated photoreceptor E.

#### Cyano Compound:



#### Polycarbonate Resin:



#### EXAMPLE 4

Photoreceptor F was prepared in the same manner as in Example 3, except for changing the thickness of the charge transporting layer to 23 μm.

#### EXAMPLE 5

Photoreceptor G was prepared in the same manner as in Example 3, except for changing the thickness of the charge transporting layer to 25 μm.

Each of photoreceptors E to G was fitted to an experimentally prepared laser printer using a reversal liquid development system, and printing was carried out while varying the developing contrast potential between 400 V and 600 V. The printed image quality was evaluated in terms of white background stains (fog) according to the following rating system. The results of the evaluation are shown in Table 3 below.



Rating System:

	Excellent	Very satisfactory with no fog
	Good	Satisfactory
5	Medium	Fairly good while partly suffering from fog
	Poor	Overall fog
	Very poor	Overall fog and very low contrast to the black image area

TABLE 3

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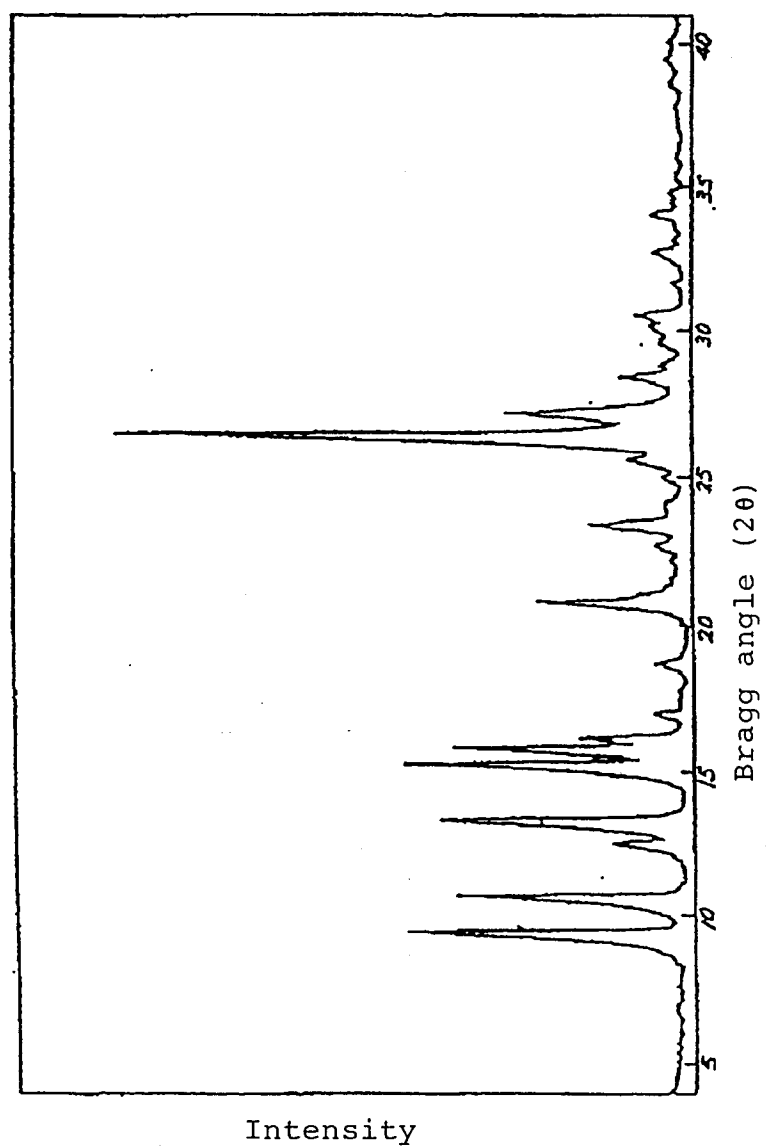
15

Photoreceptor	Developing contrast potential		
	600 V	500 V	400 V
E	good	good	excellent
F	good	excellent	excellent
G	excellent	excellent	excellent

20 **Claims**

1. An electrophotographic photoreceptor for liquid development comprising a conductive substrate having thereon at least a photoconductive layer containing a charge transporting material, said charge transporting material having a solubility in toluene of not more than about 13% by weight at 25 °C.
2. An electrophotographic photoreceptor for liquid development comprising a conductive substrate having thereon at least a photoconductive layer containing a charge transporting material, said charge transporting material having a glass transition temperature of not lower than 50 °C.
3. An electrophotographic photoreceptor for liquid development as claimed in Claim 1 or 2, wherein said photoconductive layer has a laminate structure comprising at least a charge generating layer and a charge transporting layer, and said charge transporting material is contained in said charge transporting layer.
4. An electrophotographic photoreceptor for liquid development as claimed in Claim 1 or 2, wherein said conductive substrate comprises aluminum or an aluminum alloy having thereon an anodized film.
5. An electrophotographic photoreceptor for liquid development as claimed in Claim 1 or 2, wherein said charge transporting material is a compound having a hydrazone structure.
6. An electrophotographic photoreceptor for liquid development as claimed in Claim 1 or 2, wherein said charge transporting material is an aromatic amine compound.

Fig. 1





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 94 10 4886

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-5 004 663 (SANTOKH S. BADESHA ET AL.) * column 3, line 64 - line 68 * * column 5, line 1 - line 15 * * column 6, line 3 - line 9 * * column 8, line 7 - line 14; claims 1-4 * ---	1,3,4,6	G03G5/047 G03G5/06
A	FR-A-2 647 563 (JAPAT LTD.) * page 28, compound 80 * * page 43, line 11 - line 21 * * page 47, line 27 - line 30; claim 1 * ---	1,3-5	
A	EP-A-0 511 664 (MITSUBISHI KASEI CORPORATION) * page 11, compound (1-21) * * page 36, line 16 - line 20; claim 1 * ---	1,3-6	
A	EP-A-0 504 794 (CANON KABUSHIKI KAISHA) * page 16, compound (1)-9 * * page 18, compound (1)-16 * * page 22, compound (1)-39 * * page 26, compound (2)-20 * * page 27, compound (2)-21 * * page 30, compound (2)-38 * * page 33, compound (2)-53 * * page 46, line 26 - line 31; claim 1 * -----	1,3-6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 July 1994	Examiner Hindia, E
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