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(54) **Photoreceptor for electrophotography**

Photorezeptor für Elektrophotographie

Photorécepteur pour électrophotographie

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US-A- 5 382 489

- **PATENT ABSTRACTS OF JAPAN vol. 95, no. 001 & JP-A-07 013364 (RICOH CO LTD), 17 January 1995,**
- **PATENT ABSTRACTS OF JAPAN vol. 95, no. 005 & JP-A-07 128877 (RICOH CO LTD), 19 May 1995,**
- **PATENT ABSTRACTS OF JAPAN vol. 017, no. 390 (P-1577), 21 July 1993 & JP-A-05 066577 (RICOH CO LTD), 19 March 1993,**

EP 0 744 666 B1

Description

Technical Field of Invention

[0001] The present invention relates to a photoreceptor for elctrophotography having excellent durability, a method of manufacturing thereof, an electrophotographic apparatus and an apparatus unit.

Background of the Invention

[0002] Generally, in order to carry out image formation by electrophotography, first, a toner image is formed on a photoreceptor by uniformly electrifying and imagewise exposing the surface of said photoreceptor to light, and forming a toner image by development, transferring said toner image onto a transfer material, fixing the toner image to the transfer material, to obtain an image. At the same time, the photoreceptor after completion of transfer is subjected to cleaning and de-electrification, to remove toner particles and electrostatic charge remaining on the surface of the photoreceptor. Thus the photoreceptor is provided for the subsequent electrophotographic use for a long time.

[0003] Accordingly, as the above-mentioned photoreceptor, it is usually necessary for the photoreceptor not only to have sufficient electrophotographic properties such as electrification potential, sensitivity, dark decay and remaining electrical potential property, etc., but also properties such as durability upon repeated printing, anti-abrasion property, water-proof, and durability against ozone or image exposure, etc. are required.

[0004] The photoreceptor inorganic photoreceptors, such as amorphous silicon, selenium, cadmium sulfide have been used popularly, however, in recent years, organic photosensitive photoreceptors have become the main current for their reduced cost, non-poisonous property, easy processability and wide selectivity depending on the objective.

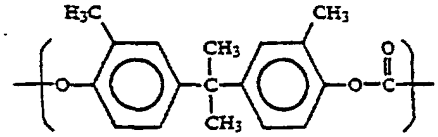
[0005] Physical fatigue and deterioration of these photoreceptors are considered to be attributed to abrasion and injury of the surface of the photoreceptor in the steps of transfer, separation, and cleaning of remaining toner particles after transfer, and decomposition or quality changes of the photoreceptor surface in the steps of electrification, image exposure and de-electrification, etc.

[0006] Accordingly. in order to prevent fatigue and deterioration of the photoreceptor, amelioration of the surface properties of the photoreceptor is important. Particularly, the photosensitive layer of organic photoreceptors are relatively softer than those of the inorganic photoreceptors, and because wearing and deterioration during repeated use of the photoreceptors are relatively large because of their organic properties, and, thus, amelioration of the surface properties of the organic photoreceptors are more important.

[0007] While such a technique that molecular weight of the binder is made large for the purpose of improving the mechanical strength of the outermost layer of the photoreceptor, the large molecular weight binder necessitate the severe drying condition since the twisting degree of the molecules is large and the viscosity of the coating composition is high. The remaining solvent in the photosensitive layer is not favorable in view of the characteristics of the photoreceptor since it causes raising potential, i.e., lowering the sensitivity, when used repeatedly.

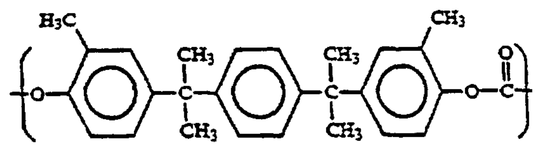
[0008] JP-A-7013364 discloses an electrophotographic photoreceptor wherein a charge generating layer (d) and a charge transporting layer (c) serving as photosensitive layers are provided on a conductive supporting body (a), and a binding resin contained in the uppermost charge transporting layer (c) has viscosity average molecular weight of 350000 or more, while a solvent having a boiling point of 135°C or more is contained in the uppermost layer (c) at 100-10000 ppm to the whole amount of the photosensitive layer.

[0009] US-A-5 382 489 discloses an electrophotographic photoreceptor comprising a conductive substrate having formed thereon a photosensitive layer containing, as binder resins, (A) a polycarbonate resin comprising a recurring unit represented by formula (I):



(I)

and (B) a polycarbonate resin comprising a recurring unit represented by formula (II) or (III):



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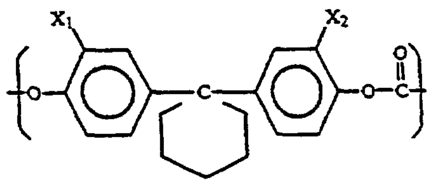
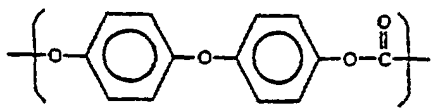


(III)

wherein X_1 and X_2 each represent a hydrogen atom or an alkyl group, or (B') a copolycarbonate resin comprising a recurring unit represented by formula (II) and a recurring unit represented by formula (IV):



(IV)

said polycarbonate resin (B) or copolycarbonate resin (B') having a lower molecular weight than that of said polycarbonate resin (A).

Summary of the Invention

[0010] Objective of the present invention is, accordingly, to provide a photoreceptor for electrophotography having enhanced durability, without causing insufficient cleaning.

[0011] Another objective of the present invention is to provide an electrophotographic apparatus by the use of the above-mentioned photoreceptor and an apparatus unit, by the use of which stable and repeated image formation is possible without causing insufficient cleaning and without exchanging the photoreceptor.

[0012] The photoreceptor of the present invention and its preferable embodiment is disclosed.

[0013] The photoreceptor comprises a photosensitive layer on an electro-conductive support, said photosensitive layer comprises a charge transport layer comprising a second charge transport layer which is an outermost surface layer of said photoreceptor and a first charge transport layer which is provided beneath said second charge transport layer, a carrier transport material being contained in each charge transport layer,

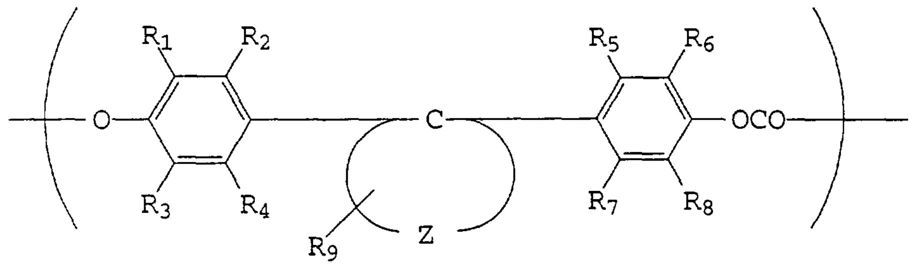
> wherein said second charge transport layer comprises polycarbonate resin having second viscometric average molecular weight of at least 40,000 and said first charge transport layer comprises polycarbonate resin having first viscometric average molecular weight being not greater than said second viscometric average molecular weight, and
>
> an amount of solvent remaining in said photosensitive layer is not more than 2% by weight of said photosensitive layer.

[0014] The viscometric average molecular weight of the polycarbonate resin is preferably greater than 100,000.

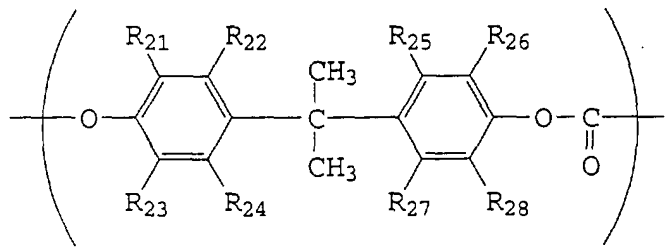
[0015] The photosensitive layer is composed of a charge generation layer and a plurality of charge transport layers provided on the charge generation layer.

[0016] The polycarbonate resin is preferably that having a structural unit represented by the general formula I or II below:

General Formula I



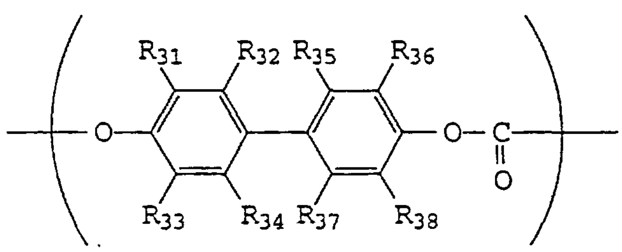
General Formula II



[0017] In the formulae, R_1 through R_8 and R_{21} through R_{28} independently represent an atom or a group selected from a group consisting of: a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group and an aryl group, provided that these groups respectively have 1 to 10 carbon atoms and may be either substituted or unsubstituted; Z represents an atomic group forming a saturated or unsaturated carbon cycle having 4 to 11 carbon atoms, R_9 represents an alkyl group or an aryl group having 1 to 9 carbon atoms.

[0018] Another preferable example of the polycarbonate resin is that having a structural unit represented by the general formula III below:

General Formula III



[0019] In the formula, R_{31} through R_{38} independently represent an atom or a group selected from a group consisting of: a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group and an aryl group, provided that these groups respectively have 1 to 10 carbon atoms and they may be either substituted or unsubstituted.

[0020] The viscometric average molecular weight of the polycarbonate resin incorporated in the first charge transport layer provided beneath the outermost surface layer of the photoreceptor for electro-photography is preferably not greater than 50,000.

[0021] The outermost surface layer of said photoreceptor for electro-photography preferably comprises silica particles, of which value of heat absorption energy change ΔH controlled under humidity condition at 80% within the temperature range between 40° and 200°C is 0 to 20 Joule/g; and the volume average particle diameter is not smaller than 0.05 μm and not greater than 2 μm.

Brief Explanation of the Drawing

[0022]

Fig. 1
A cross-sectional drawing illustrating the layer structure of the photoreceptor according to the present invention.
Fig. 2
A cross-sectional drawing illustrating the image forming apparatus according to the present invention.
Fig. 3
A longitudinal sectional view of the coating apparatus used in the present invention.
Fig. 4
A perspective view of the coating apparatus used in the present invention.

Detailed disclosure of the Invention

[0023] The outermost surface layer of the photoreceptor denotes the layer which constitutes the outermost layer at the time of completion of manufacturing of the photoreceptor, and it is a charge transport layer (CTL). In the outermost surface layer, silica particles, CTM, which are incorporated, and other additives may be dispersed in the binder resin, as to which explanation is made hereinbelow, and provided by means of coating, etc.

[0024] Polycarbonate resin used in the present invention is explained. The preferable polycarbonate resin are those having structural units represented by the above-mentioned general formulae I, II and III, and, especially resins with the viscometric average molecular weight of 40,000 or greater are used. Particularly, resins of which viscometric average molecular weight of 100,000 to 500,000 are preferable.

[0025] As R_1 through R_8, R_{21} through R_{28} and R_{31} through R_{38}, hydrogen atom or an alkyl group of one to three carbon atoms are preferable. Examples of Z are unsubstituted cycxlopentyl ring and cyclohexyl ring. These polycarbonate resins may be either a homopolymer consisting only of the structural unit represented by the general formula I, II or III, or a copolymer or a block polymer containing other copolymerization unit. In the case of a copolymer or a block polymer, those consisting of the structural units I, II and III in combination are preferable.

[0026] These polycarbonate resins are easily available as good on the market. An example of resins having a structural unit of the general formula I is BPZ, i.e., poly(4,4'-cyclohexylidene diphenyl)carbonate, which is in the market as TS-2050:a product of Teijin, and Z-800:a product of Mitsubishi Gas Co., Ltd., etc. As polycarbonate resins having a structural unit of the general formula II, BPA, i.e., poly(4,4'-isopropylidenediphenyl) carbonate, is exemplified, and, more specifically, ML-5237:a product of GE Plastics Ltd., etc. are in the market. As polycarbonate resins having a structural unit of the general formula (III), BPPC, i.e., poly(4,4'-diphenyl)carbonate, etc. are exemplified.

[0027] As solvents or dispersion media for these polycarbonate resins, for example, n-butylamine, diethylamine, isopropanolamine, triethanolamine, triethylenediamine, N,N-dimethylformamide, acetone, methylethylketone, methylisopropylketone, cyclohexanone, benzene, toluene, xylene, chloroform, dichloro methane, 1,2-dichloroethane, 1,2-dichloropropane, 1,1,2 -trichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethane, tetrahydrofurane, dioxane, methanol, ethanol, isopropanol, ethyl acetate, butyl acetate, dimethylsulfoxyd, methylcellosolve, etc. can be mentioned. These solvents may be used either singly or two ore more kinds in combination.

[0028] Next, silica particles which may be used in the present invention are explained. The silica particles are preferably those with the volume average particle diameter of not less than 0.05 and not more than 2μm, and, more preferably not smaller than 0.1, and not greater than 2 μm. In addition, particles having narrow particle size distribution are preferable.

[0029] The volume average particle diameter is preferably not smaller than 0.05 μm, to make ensure required surface strength of the photoreceptor, so that the photoreceptor does become liable to be injured by abrasion and the electrophotographic properties are maintained. It does not succeed 2 μm, so that the surface of the photoreceptor is kept with appropriate roughness, without causing insufficient cleaning.

[0030] Further, it is preferable that the silica particles have a spherical shape, in particular, ones of which long diameter to short diameter ratio is less than 2.0, is preferable. Herein, the term "spherical shape" means that when the image by an electron microscope is enlarged to an extent under which the shape of the fine particle is not of an infinite shape, but of a spherical shape. In that case, friction coefficient of the surface of the photoreceptor can be lowered, and there is an advantage that turning-up of the resilient cleaning blade, which has heretofore been considered to be a problem, can be prevented.

[0031] As for the method of manufacturing the silica particles, CVD method or chemical vapor deposition method is preferable. This method includes step of producing a high temperature flame by burning a oxygen-hydrogen mixed gas or a hydrocarbon-oxygen mixed gas, and causes a gas phase reaction in this gas, to obtain silica particles, and as an example, a method of obtaining silica particles by undergoing silane gas a gas phase reaction in the high temperature flame of the above-mentioned mixed gas has been known.

[0032] The silica particles is preferably manufactured by means of the above-mentioned CVD method, however, inter alia, it is particularly preferable to manufacture it by putting metallic silicon powder into the above-mentioned mixed gas, and, then, let it burn explosively.

[0033] Details of this method is described in, for example, in Japanese Patent O.P.I. Publication Nos. 60-255602, 5-193908, 5-193909, 5-193910, 5-193928, 5-196614 and 6-107406.

[0034] In the manufacturing methods, silicon metal raw material is provisionally washed with highly purified water for several times, to remove soluble ingredients, and, then, removing gaseous constituents by heat treatment, to obtain highly purified silicon powder. Next, highly purified silica particles are obtained by introducing a flammable gas such as LPG and a combustion aiding gas such as oxygen gas to a burner arranged on the top of a manufacturing apparatus, to form a fire for ignition, and, then, introducing a carrier gas, containing in dispersion the above-mentioned highly purified silicon powder, to initiate combustion. Thereafter, the above-mentioned supporting gas is supplied on a multistep basis and explosively burn the above-mentioned silicon powder by oxidation, to obtain highly purified silica particles.

[0035] According to the above-mentioned manufacturing method, not only highly purified fine silica particles, with narrow particle size distribution are obtained, but also it is possible that the above-mentioned particle size distribution can be varied to a wide extent depending upon objectives.

[0036] The volume average particle diameter of the silica particles can be measured by the use of a laser diffraction light scattering particle size distribution measuring apparatus LA-700, a product of Horiba Manufacturing Co., Ltd.

[0037] Differential thermal scanning calorimetry of the silica particles can be obtained quantitatively by the following equation, which is derived from the rule that a peak area of DSC is proportional to absorbed thermal energy in the method of adding energy in order to eliminate temperature differences between a thermally stable standard material and a sample, when the sample is heated at a constant rate.

$$M \cdot \Delta H = K \cdot A$$

[0038] Herein, M denotes mass of the sample; ΔH denotes amount of energy change of the sample per a unit mass; K denotes a constant decided depending on the apparatus; and a denotes the peak area. The silica particles were humidified under 80% RH condition for 24 hours. Thereafter they were kept under the same condition in a sealed container, and measurement was carried out within 60 minutes after completion of humidification.

[0039] Conditions for the DSC measurement applied to the present invention are as follows:

Apparatus:

Differential thermal scanning calorimeter DSC-20
Thermal Controller SSC-580(a product of Seiko
Denshi Kogyo co., Ltd.

Conditions for measurement:

Temperature: 35 to 300°C
Temperature elevation rate; 10°C/min. at 80% RH)
Measurement surroundings: Static air atmosphere

[0040] Preferable ΔH of the silica particles according to the present invention is between 0 and 20 joules/g, and, more preferably, between 0.1 and 10 Joules/g.

[0041] The silica particles are incorporated in the outermost surface layer of the photoreceptor together with a binder, and the proportion of the silica particles in the outermost surface layer with respect to the binder is, usually 1 to 200% by weight and, more preferably between 5 and 100% by weight.

[0042] The photosensitive layer of the photoreceptor may be an inorganic photoreceptor which is formed of by incorporating the above-mentioned silica particles and organic particles in the outermost surface layer, however, it preferably is an organic photoreceptor which comprises an organic charge generation material (CGM) and an organic charge transport material (CTM). Layer structure of said organic photoreceptor is shown in Fig. 1.

[0043] Fig. 1 (A) illustrates a photoreceptor having a photosensitive layer 6, consisting of a single layer structure, which comprises both the charge generation material (CGM) and the charge transport material (CTM) on an electroconductive support 1 through an intermediate layer 2. Fig. 1 (B) illustrates a photoreceptor which comprises on an electro-conductive support 1 and, laminated thereon through an intermediate layer 2 a photosensitive layer 6 consisting of charge transport layer (CTL) 3 containing as its main constituent a charge transport material (CTM), and a charge generation layer (CGL) 4 containing as its main constituent a charge generation material (CGM).in this order. Fig. 1 (C) illustrates a photoreceptor which comprises on an electro-conductive support 1 and, laminated thereon through an intermediate layer 2 a photosensitive layer 6 consisting of a charge generation layer (CGL) 4 and a charge transport layer (CTL) 3 in this order.

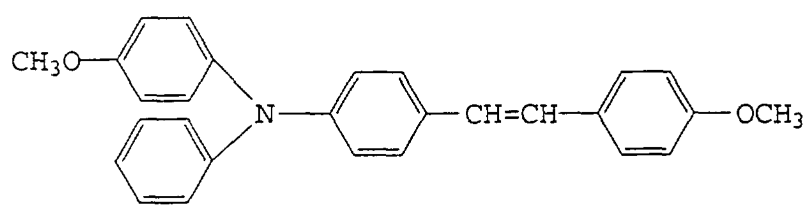
[0044] Further, Figs. 1 (D), 1 (E) and 1 (F) illustrate structures, in which a protective layer 5 is provided on the photosensitive layer 6 of Figs. 1 (A), 1 (B) and 1 (C), respectively. The above-mentioned respective Figs. 1 (A) through 1 (F) illustrate typical layer structures. The intermediate layer shown in these drawings may, whenever it is unnecessary, be omitted.

[0045] As charge generation materials (CGM) used in the photosensitive layer 6 of the respective photoreceptors as shown in Fig. 1 (A) through 1 (F), for example, phthalocyanine pigments, polycyclic quinone pigments, azo pigments, perylene pigments, indigo pigments, quinacridone pigments, azulenium pigments, squalerium dyes, cyanine dyes, pyrilium dyes, thiopyrilium dyes, xanthane dyes, triphenylmethane dyes and stilyl dyes can be mentioned, and these charge generation materials are used either singly or in combination with an appropriate binder resin to form a layer.

[0046] As charge transport materials (CTM) which are incorporated in the above-mentioned photosensitive layer, for example, oxazole derivatives, oxadiazole derivatives, thiazole derivatives, thiadiazole derivatives, triazole derivatives, imidazole derivatives, imidazolone derivatives, imidazoline derivatives, bisimidazolidine derivatives, stilyl compounds, hydrazone compounds, benzidine compounds, pyrazoline derivatives, stilbene compounds, amine derivatives, oxazolone derivatives, benzothiazole derivatives, benzimidazole derivatives, quinazoline derivatives, benzfurane derivatives, acridine derivatives, phenadine derivatives, aminostilbene derivatives, poly-N-vinylcarbazole, poly-1-vinylpypyrene, and poly-9-vinylanthracene, etc. can be mentioned, and these charge transport materials (CTM) are used to form a layer together with a binder.

[0047] Among these the following compounds can be mentioned as particularly preferable charge transport materials (CTM).

(T-1)



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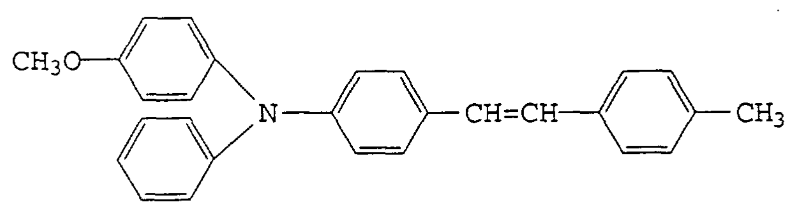

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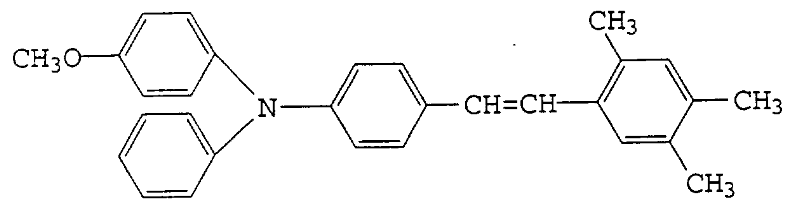
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CH3
CH3

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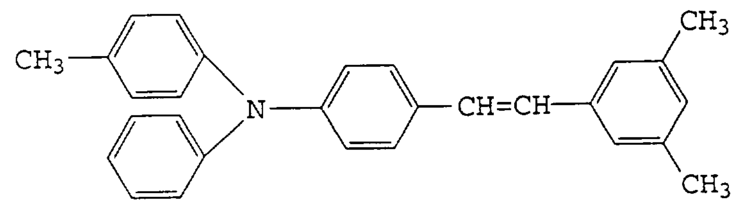
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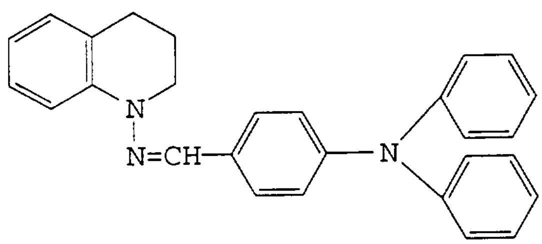
(T-5)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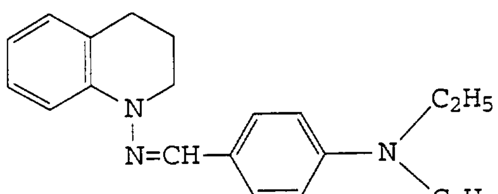
(T-6)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C2H5

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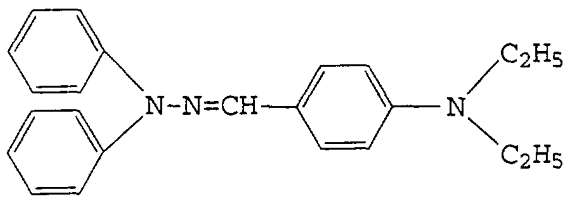
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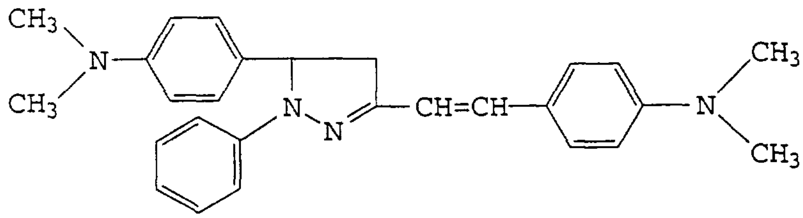
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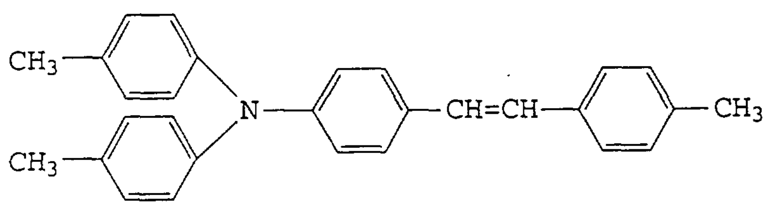
(T-9)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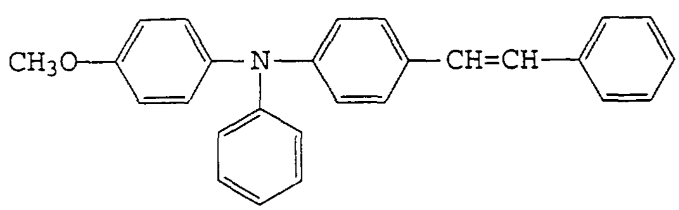
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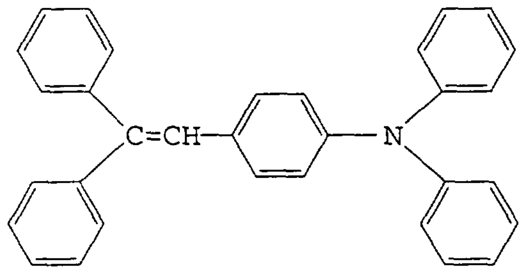

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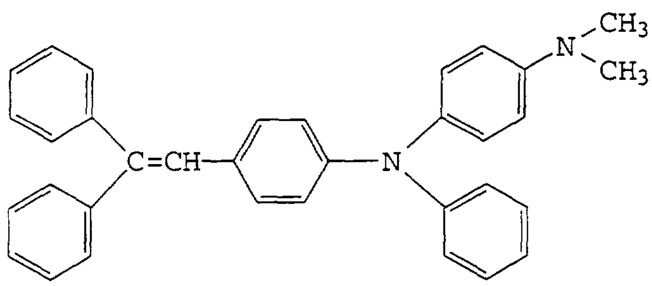

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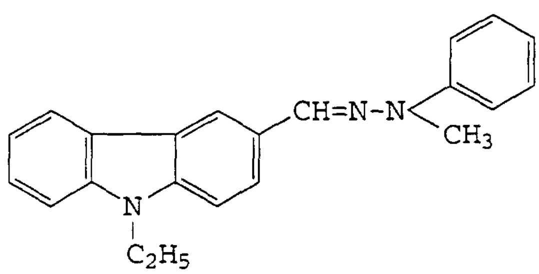

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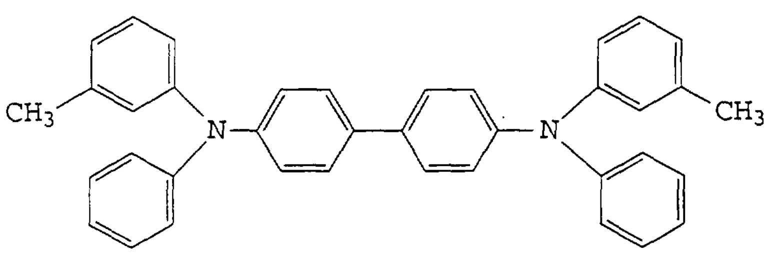

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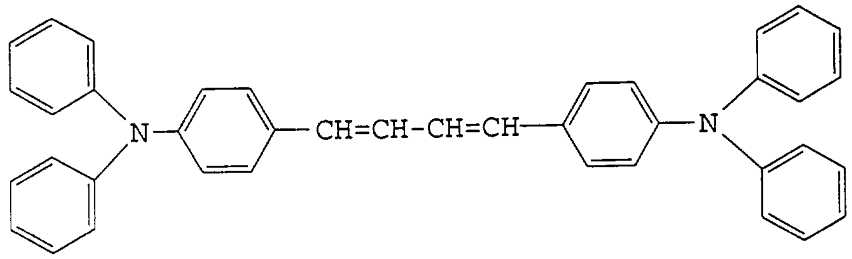

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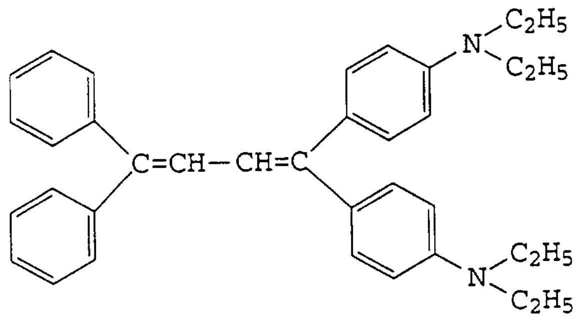

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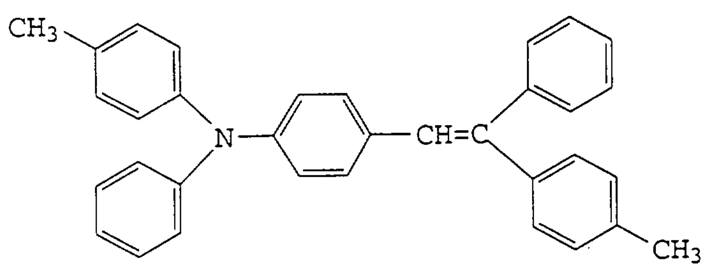

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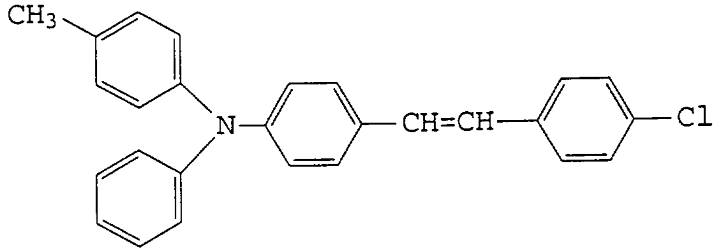

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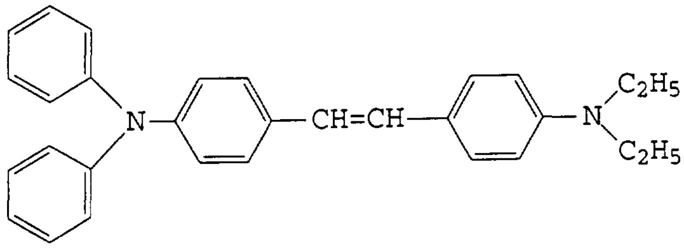

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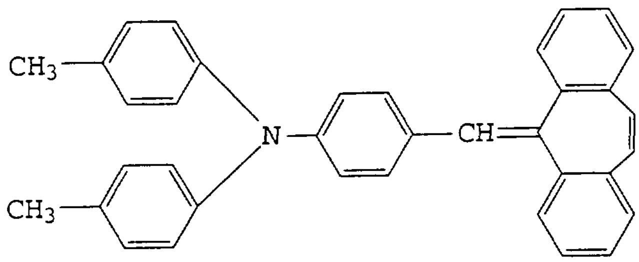

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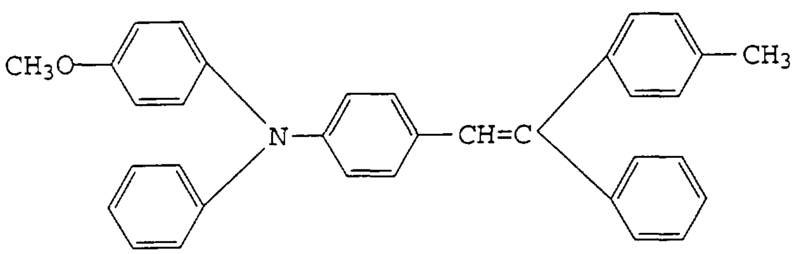

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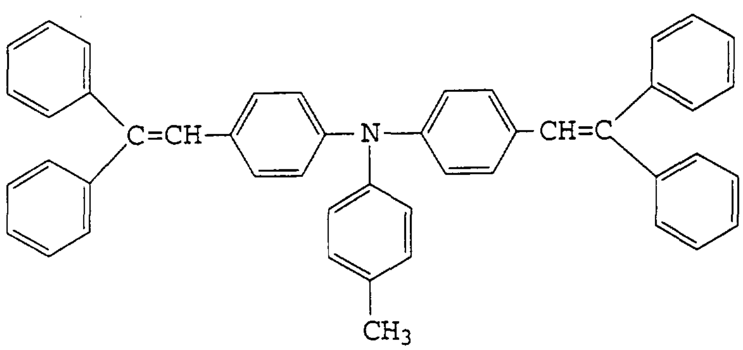

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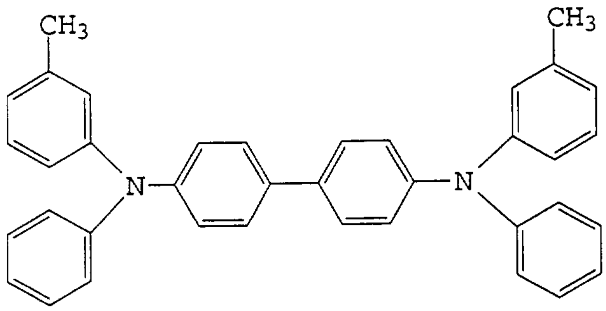

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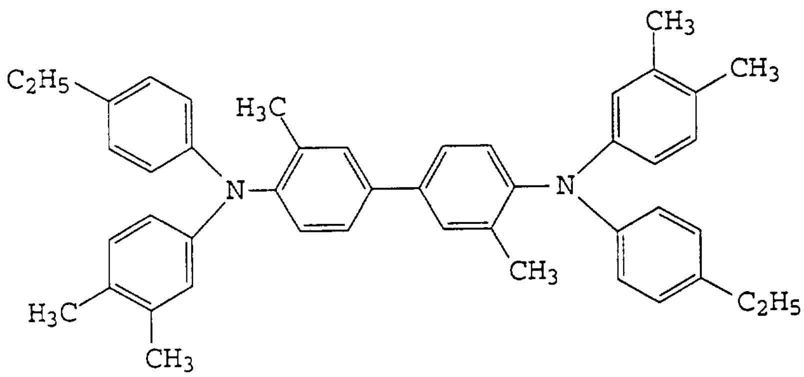

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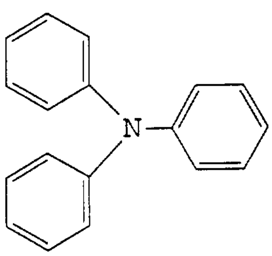

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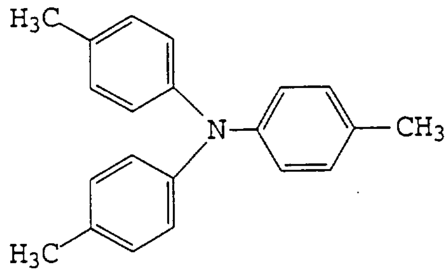

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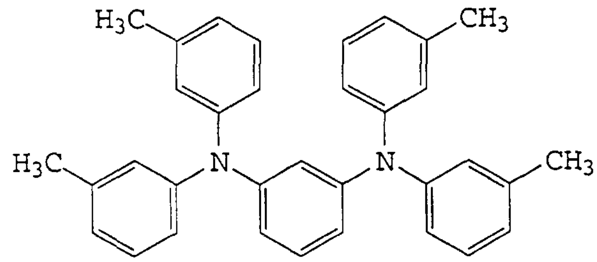

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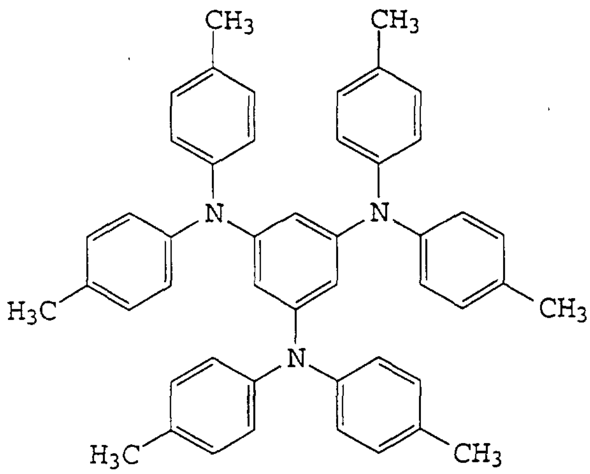

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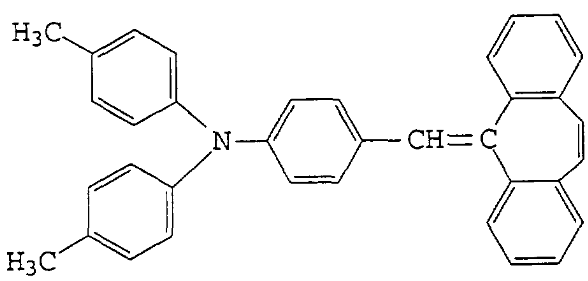

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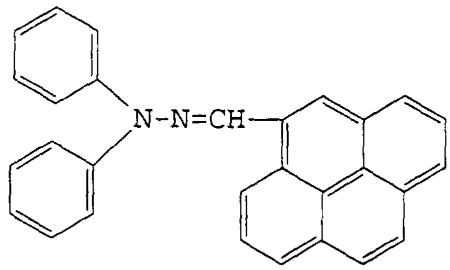


[0048] As binder resin to be incorporated in the photosensitive layer 6, or the charge generation layer (CGL) or the charge transport layer (CTL), polyester resins, polystyrene resins, methacrylic resins, polyvinyl chloride resins, polycarbonate resins, polyvinyl butyral resins, polyvinyl acetate resins, styrene-butadiene resins, vinylidene chloride-acrylonitrile copolymer resins, vinyl chloride-maleic acid anhydride resins, urethane resins, silicon resins, epoxy resins, silicon-alkyd resins phenol resins, polysilane resins polyvinyl carbazole resins, etc. are exemplified.

[0049] Next, as solvent or media, which are used when the above-mentioned respective layers are formed, those that are referred to as the solvent or the medium for the polycarbonate resin may preferably be used. When a ketone-type solvent is used, still preferable sensitivity potential stability during repeated use, etc. may be still improved. Further, these solvents can be used either singly or two or more kinds in combination.

[0050] The mixing ratio of the charge generation material and the binder resin in the charge generation layer is preferably 1:5 to 5:1, and particularly preferably 1:2 to 3:1. Thickness of the charge generation layer is preferably less than 5 μm and, in particular, 0.05 to 2 μm. Still further, it is preferable that remaining amount of the solvent in the charge generation layer is not more than 2% by weight.

[0051] The charge generation layer can be formed by coating a composition prepared by dissolving the above-mentioned charge generation material and the binder resin in an appropriate solvent, and drying it. Mixing proportion between the charge generation material and the binder resin is preferably 3:1 to 1:3, and particularly preferably, 2:1 to 1:2.

[0052] When a plurality of charge transport layers are provided, it is usually preferable that the weight mixing ratio of the charge transport material and the binder resin in the uppermost charge transport layer is smaller than those in the layers located under said uppermost charge transport layer. By this construction, it becomes possible to enhance mechanical strength without losing sensitivity performance.

[0053] Further, the binder resin to be incorporated in the charge transport under the outermost surface layer, is made to be a polycarbonate resin of which viscometric average molecular weight is smaller than that of the resin incorporated in said outermost surface layer, so that it becomes possible to reduce the amount of the remaining solvent and, as a result, potential stability during repeated use can be improved. Still further, the viscometric average molecular weight of the binder contained in the charge transport layer located under the outermost surface layer is preferably smaller than 50,000, and still more preferably, it is a polycarbonate resin whose viscometric average molecular weight is between 20,000 and 40,000.

[0054] Preferable thickness of the charge transport layer is usually 5 to 50 μm and, in particular, 10 to 40 μm. When a plurality of charge transport layers are provided, preferable thickness of the charge transport layer located at the uppermost position is not more than 10 μm, and , it is preferable the thickness is smaller than the total thickness of all charge transfer layers provided under the thickness of the layer provided just beneath the outermost surface layer.

[0055] The photoreceptor according to the present invention is manufactured, as mentioned above, by coating and drying predetermined layers, the amount of solvent remaining after drying is not more than 2%, and, more preferably, not more than 1.5% by weight with respect to the photosensitive layer. In order to regulate the amount of remaining solvent within the above-mentioned level, the photosensitive layer is dried at 90 to 120 °C, and, more preferably at 95 to 120 °C. When the amount of remaining solvent is regulated within the above-mentioned level, repeating property of the photoreceptor may be improved. Further there is an advantage that turning-up of the resilient cleaning blade, which has heretofore been considered to be a problem, can be prevented.

[0056] As an electroconductive support for the photoreceptor,

1) a metal plate such as an aluminum plate or a stainless steel plate;
2)supports consisting of a plastic support and a thin metal layer made of, aluminum, paradium, gold, etc., which is provided thereon by evaporation or lamination; and

3) paper or plastic film support provided thereon a layer of an electroconductive compound such as a electro-conductive polymer, indium oxide, tin oxide, etc. by coating or evaporation method, etc. are exemplified.

[0057] Next, as methods of coating process in order to manufacture the electro-photographic photoreceptor, dip coating, spray coating, ring-shaped coating amount regulating coating, etc. may be applied, however in the coating process of the lower layer of the photosensitive layers, it is preferable to use the spray coating process or the ring-shaped coating amount regulating coating process in order not to dissolve lower layers of the photosensitive layer as much as possible, and in order to attain uniform coating. There is detailed description on the above-mentioned spray coating in Japanese Patent O.P.I. Publication Nos. 3-90250 and 3-269238. With reference to the above-mentioned ring-shaped coating amount regulating coating method, there is detail description is made in, for example, Japanese Patent O.P.I. Publication No. 58-189061. Particularly, when the viscometric average molecular weight becomes greater and so the viscometric of the coating composition is increased, sufficient fluidity in the coating composition may not be obtainable, and this often causes uneven coating in case by dip coating or spray coating. But by the use of a ring-shaped amount regulating coating method, even coating without causing uneven coating becomes possible.

[0058] In the present invention, coating of the coating composition containing the polycarbonate resin, of which viscometric average molecular weight is more than 100,000, is carried out by the use of a ring-shaped coating amount regulating coating apparatus. In the ring-shaped coating amount regulating coating apparatus, for example, as shown in Fig. 3, a cylindrical member 51A and 51B is continuously shifted upward to the direction of an arrow along the center line XX, and a coating composition L is coated by the portion 60, which is directly concerned in coating and is herein referred to as coating head. In this coating method, materials used for the support, other than hollow drums such as aluminum drums, or plastic drums, seamless belt-type substrata may also be used. In the above-mentioned coating head 60, distributing slits 62, which is herein referred to simply as "slit"", have been formed in the horizontal direction. This slit 62 is connected to a loop-shaped distribution chamber 63 for the coating composition, and into this distribution chamber a light-sensitive composition L preserved in a reservoir 63 is supplied through a supply tube 64 by a compression pump 55. On the other hand, below the outlet-mouth for the coating composition, in the downstream of the out-let mouth 61 for the coating composition, an inclined surface 65 is formed so that it is continuously inclined downward, and terminated with a dimension a little larger than outer end of the support. Further, a lip-shaped portion 66 has been formed from the edge of the inclined surface 65 and extends downward. In the coating by the use of this type of coating apparatus, in the step of drawing up the support 51, the coating composition L is pushed out from the slit 62, and flow down along the inclined surface 65. when the light-sensitive composition. Excess light-sensitive composition is discharged from the discharging outlet 67.

[0059] Since the edge of the inclined surface and the support are disposed with an appropriate clearance to each other, coating can be performed without injuring the support, and without injuring an prior coated layer or in the case where a plurality of layers having different natures are formed.

[0060] Further, according to a coating method using the ring-shaped coating amount regulating coating apparatus since the edge of the inclined surface and the support are disposed with an appropriate clearance to each other, coating can be performed without injuring the support, and without injuring an prior coated layer in the cases where multiple layers, which have different properties and are soluble in the same solvent, because of shorter time of presence in the solvent in comparison with the case of the dip coating, ingredients of the lower layer seldom dissolute out into the upper layer, and coating can be conducted without effluence into the coating bath.

[0061] The coating method using the ring-shaped coating amount regulation-type coater is effectively applied to film formation on the circumferential surface of a photosensitive drum for electrophotography. That is to say, this type of coating machine is employed in the coating on the circumferential endless surface of drum support. In the coating, either the support or the coating machine may be moved. Further, the cylindrical support nay also be rotated.

[0062] In accordance with the above-mentioned spray coating or ring-shaped coating amount regulating-type coating method, in comparison with the above-mentioned dip coating, uniform and even coating can be attained without unnecessary consumption of the coating composition, and without solubilizing and injuring the layer provided thereunder.

[0063] According to one of embodiments of the present invention, a subbing layer, having a barrier function as well as a resin function, can be provided between the electroconductive support and the photosensitive layer.

[0064] As materials used for the subbing layer, casein, polyvinyl alcohol, nitrocellulose, styrene-acrylic acid copolymers, polyvinyl butyrals, phenol resin polyamides such as nylon-6, nylon-66, nylon-610, nylon copolymers, alkoxymethylated nylon, etc.; polyurethane, gelatin, aluminum oxides, etc. can be mentioned. Thickness of the subbing layer is preferably 0.1 to 10 μm and, particularly 0.1 to 5 μm.

[0065] Further, it is possible to provide a coating between the support and the subbing layer in order to compensate surface defects of the support, or an electroconductive layer for the purpose of preventing occurrence of interference fringes, which is a problem in the case where the image input is carried out with laser. This electroconductive layer can be prepared by coating and drying a composition containing a binder, in which appropriate conductive particles such as carbon black, metal particles, etc. have been dispersed. Preferable thickness of this electroconductive layer is 5 to 40 μm and, particularly, 10 to 30 μm.

[0066] Moreover, the shape of the support may be either of a drum, sheet or a belt, and it is preferable that a shape which is most suitable for the electrophotographic apparatus, to which it is to be applied.

[0067] The image carrying member according to the present invention is one, which is widely applicable to conventional electrophotographic apparatuses such as not only copying machines, laser printers, LED printers, liquid crystal shutter-type printers, etc., but also to other apparatuses such as displays, recording apparatuses, printing, photolithographic, and facsimile apparatuses, in which electrophotographic technology has been employed.

[0068] A conceptual structure of an image-forming apparatus comprising the electrophotographic photoreceptor according to the present invention is shown in Fig. 2.

[0069] In Fig. 2, numerical symbol 10 denotes a photoreceptor drum, which is an image carrying member, coated with an OPC photosensitive layer, grounded and is rotarily driven clockwise. Numerical symbol 12 denotes a scorotron charging device, by which the peripheral surface of the photoreceptor 10 is uniformly electrified. Prior to this electrification by the use of this charging device, de-electrification of electric charge remaining on the peripheral surface of the photoreceptor by conducting light exposure by the use of an exposure section 11, to eliminate history of the photoreceptor in the previous image forming process.

[0070] After uniform electrification on the photoreceptor, imagewise exposure based on image signals is carried out by the use of an exposing means 13. The image exposing means 13 in this drawing is equipped with a laser diode, which is not shown in the drawing, as an illuminating light source, and an electrostatic latent image is formed by light scanning on the surface of the photoreceptor by a reflection mirror 132 through a rotating polygon mirror, an f·θ lens, etc.

[0071] This electrostatic latent image is, then, developed with a developing device 14. Around the periphery of the photosensitive drum 10, a developing device 14 consisting of four kinds of developers, which consist of yellow (Y) toner and carrier, magenta (M) toner and carrier, cyan (C) toner and carrier, and black (K) toner and carrier, respectively, and, then, first, development with a first color is carried out with a development sleeve 141, which comprises built-in magnets therein and rotates, while carrying the first developer. The developer comprises carrier particles consisting of ferrite as core and a resin coated thereon, and toner particles consisting of a polyester resin as the main ingredient and, incorporated therein as additives, a pigment, a charge controlling agent silica, titanium oxide, etc. depending on the color to be produced. The developer, after being formed into a layer having thickness of 100 to 600 μm on the development sleeve 141 by the layer forming means and is transported to a development domain, at which development is carried out. At this time development is usually performed while applying direct current or alternating electric current between the photosensitive drum 10 and the development sleeve 141.

[0072] In the color image formation process, after development of the first color image is completed, uniform electrification is again conducted, and, then second imagewise exposure to form a second electrostatic latent image by the exposing means 13. Similar image formation process is repeated for the images of the third and fourth colors, and, thus, a developed image consisting of four different colors is formed on the peripheral surface of the photoreceptor 10.

[0073] An electrophotographic apparatus for forming black-and-white images, the developing device 14 is constructed with one black toner and an image is formed by a single development process.

[0074] Recording paper P is, after completion of image formation, and when the transfer timing is well arranged, supplied to the transfer domain by the rotary movement of a paper supplying roller 17.

[0075] In the transfer domain, transfer roller 18 is brought in pressure contact with the peripheral surface of the photoreceptor drum 10 and the multi-color image is transferred to a recording paper P, which was sandwiched and is transported to the transfer domain is transferred at one time in synchronization with the transfer timing.

[0076] Subsequently the recording paper is de-electrified by a separation brush 18 and is separated from the surface of the photoreceptor drum, to be transported to a fixing apparatus 20, where the toner is melted and fixed to the recording paper P by a heat roller 201 and a pressure roller 202, and, then, the recording paper P is discharged out of the apparatus through discharging roller 21. The above-mentioned transfer roller 18 and the separation brush 19 are, at this time, evacuated from the circumference surface of the photoreceptor drum 10, and are prepared to the subsequent toner image formation.

[0077] The photoreceptor drum 10 after separating the recording paper P, undergoes cleaning by bringing a cleaning blade 221 of a cleaning device 22, into pressure contact with the surface of the photoreceptor drum 10, thus to remove and clean the remaining toner particles. The photoreceptor drum 10 is subjected to de-electrification by 11 and electrification with the charging device 12, thus to initiate the next image formation process. In the case where color images are superimposed on the photoreceptor drum, the above-mentioned blade 221 is shifted and evacuated from the periphery of the photoreceptor drum 10 immediately after completion of cleaning.

[0078] In the drawing numerical symbol 30 denotes a cartridge in which the image carrying member, electrification means, developing means and cleaning means are assembled into one unit so that it can be mounted on and removed from the main enclosure of the electrophotographic apparatus.

[0079] As an electrophotographic apparatus, plurality of the above-mentioned structural elements such as the photoreceptor, the developing means, the cleaning means, etc. can be assembled into one apparatus unit, and this is fixed to the main enclosure of the main apparatus so that it may be freely mounted onto and removed from the main enclosure of the apparatus. For example, at least one of each of the charging means, the developing means and the cleaning means may be supported and assembled as a single unit together with the photoreceptor, and this is mounted on the main enclosure by the use of a guiding means such as a rail fixed to the main enclosure so as to be removable from it. In this case, the charging means and/or the developing means may be incorporated in the above-mentioned apparatus unit.

[0080] The image exposure means is performed, in the case where the electrophotographic apparatus is used as a duplicating machine or a printer, by irradiating reflectionlight or transmission light from an original on the photoreceptor, or by reading an original using a sensor and carrying out scanning laser beam, driving a LED array or a liquid crystal shutter array, thus to irradiate light on the photoreceptor.

[0081] When it is used as a printer of a facsimile machine, exposure means 13 is used as an exposure means for printing received data.

Example

[0082] The present invention is hereinbelow explained in detail with reference to working examples.

Examples 1 through 9 and Comparative Example 1 through 5

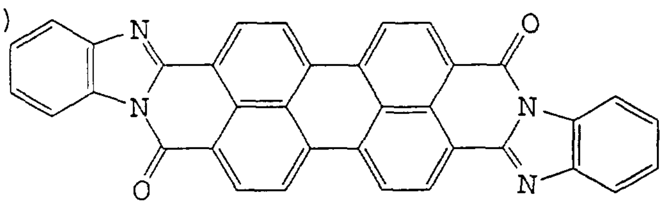
<Preparation of Photoreceptor-1 according to the present invention>

[0083] On a cylindrical drum of 80 mmϕ made of aluminum, 0.3-μm-thick intermediate layer was formed by dip coating a coating composition, prepared by dissolving 1.5 parts by weight of a copolymer-type polyamide resin "AMILAN CM-8000", a product of To-Ray Co., Ltd., in a mixed solvent consisting of 90 parts by weight of methanol and 10 parts by weight of butanol. Next, 0.8 part by weight of a polyvinyl butyral resin "ESLEC BL-S", a product of Sekisui Chemical Industry Co., Ltd., was dissolved in a mixed solvent consisting of 80 parts by weight of methylethyl ketone and 20 parts by weight of cyclohexanone, and to the thus prepared composition 4 parts by weight of CGM-1, of which CGM to binder quantity ratio is 5.0, and the chemical structure thereof is given below, was mixed and dispersed, to prepare a coating composition, This coating composition was coated on the above-mentioned intermediate layer by dip coating, and was dried, to form a 0.2-μm-thick charge generation layer.

Chemical structure of CGM-1 (a mixture of 1 and 2)

[0084]

(1)



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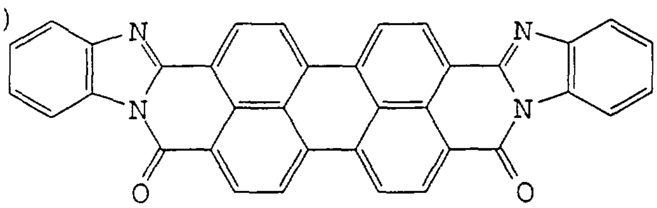


[0085] Next, 15 parts by weight of a polycarbonate resin "EUPIRON Z300, a product of Mitsubishi Gas Chemical Co., Ltd., as a binder and 10 parts by weight of Compound (T-9) as a charge transport material (CTL) were dissolved and dispersed in 100 parts by volume of methylene chloride, to prepare a coating composition. Then this coating composition was coated by dip coating method on the above-mentioned charge generation layer and was dried, to form a first charge transport layer with dry layer thickness of 25 μm.

[0086] Further, 1.5 parts by weight of a polycarbonate resin "TS-2050", a product of Teijin Chemical Industry Co., LTD., as a binder, 0.6 part by weight of inorganic particles shown in Table 1, and 1 part by weight of Compound (T-9) as the charge transport material were dissolved and dispersed in 100 parts by volume of 1,2-dichloroethane, to prepare another coating composition. This coating composition was then coated using a ring-shaped coating amount regulation-type coating machine on the above-mentioned first charge transport layer, dried at 110 °C for one hour, thus to form a 1-μm-dry-thickness second charge generation layer. Thus a Photoreceptor-1 according to the present invention, as shown in Table-1 was obtained. Amount of the remaining solvent at this time was 0.18% by weight with respect to the photosensitive layer.

<Preparation of Photoreceptors 2 through 9 according to the present invention and Comparative Photoreceptors 1 through 5>

[0087] Photoreceptors 2 through 9 according to the present invention, and Comparative Photoreceptors 1 through 5 were prepared in the same manner as Photoreceptor 1, provided upon preparation of these samples kind, molecular weight, drying temperature of the photoreceptor, amount of the remaining solvent, kind of silica particles, volume average particle size and proportion in terms of % by weight with respect to the binder were varied as those given in Table 1.

Table 1

Example No.	Binder				Inorganic Particles			
	Kind	Molecular Weight	Drying Temperature (°C)	Amount of Remaining Solvent (%)		Diameter (µm)	ΔH	Amount of Addition
Example 1	BPZ (TS-2050: made by Teijin)	50,000	110	0.18	SO-C1	0.2	6.5	40
Example 2	BPZ (Z-800: made by Mitsubishi Gas	80,000	110	0.21	SO-C1	0.2	6.5	40
Example 3	BPA (made by GE Plastic Ltd.)	200,000	110	0.37	SO-C1	0.2	6.5	40
Example 4	BPZ (TS-2050)	50,000	110	0.17	SO-C2	0.5	5.5	10
Example 5	BPZ (Z-800)	80,000	110	0.21	SO-C2	0.5	5.5	10
Example 6	BPA (GE)	200,000	110	0.37	SO-C2	0.5	5.5	10
Example 7	BPZ (Z-800)	80,000	90	1.90	SO-C1	0.2	6.5	40
Example 8	BPZ (Z-800)	80,000	100	0.87	SO-C1	0.2	6.5	40
Example 9	BPZ (Z-800)	80,000	120	0.03	SO-C1	0.2	6.5	40
Comparative example 1	BPZ (Z-800)	80,000	80	6.63	SO-C1	0.2	6.5	40
Comparative example 2	BPZ (Z-800)	80,000	80	5.94	SO-C1	0.2	6.5	10
Comparative example 3	BPZ (Z-300)	30,000	110	0.16	SO-C1	0.2	6.5	40
Comparative example 4	BPZ (Z-300)	30,000	80	2.55	SO-C1	0.2	6.5	40
Comparative example 5	BPA (K-1300)	30,000	80	4.77	SO-C1	0.2	6.5	40

[0088] Thus manufactured photoreceptors were mounted on an analogue duplicating machine Konica U-Bix Type

4145, a product of Konica Corporation, and image formation tests were carried out with respect to the respective photoreceptors under normal temperature and normal humidity (20 °C, 60%). Image evaluation, amount of potential change and reduced thickness of the photosensitive layer after 100,000-time repeated copying operation were conducted.

1) Image Evaluation.

[0089] The above-mentioned photoreceptors were mounted one by one on the above-mentioned copying machine, and 100,000-time image formation was carried out using an original having a halftone image. At this tine, Scorotron charging device was used as an electrification device and image formation was conducted while applying a constant voltage, i.e., -750V on the above-mentioned photoreceptors.

[0090] After completion of the above-mentioned 100,000 time image formation tests, occurrence of fog in the background due to insufficient cleaning, occurrence of scratch trouble due to turning up of the cleaning blade, and sharpness of the image were evaluated by visual observation. Results are shown in Table 2.

Measurement of potential variation

[0091] Electric potential values both in the solid black portion (Vb) and the solid white portion (Vw) of the image before and after the above-mentioned 100,000 time image formation tests were measured, and the amount of potential variations of the respective photoreceptors were obtained from the differences ΔVb and ΔVw.

[0092] In this example, an original having a solid black domain with reflective density at 1.3 and solid white domain with reflective density at 0.0 in halves was used, and after electrification at -750V by the use of the above-mentioned Scorotron charging device, electric potentials of the latent images formed from the above-mentioned original corresponding to the above-mentioned solid black portion (Vb) and the solid white portion (Vw) were measured.

Table 2

Embodiment No.	Potential Variation after 100,000 copies		Image Evaluation		Amount of Reduced Thickness
	$\|\Delta Vb\|$	$\|\Delta Vw\|$	Image Quality of First Copy	Image Quality of 100,000th Copy	
Example 1	24	51	Good	Good	0.8
Example 2	18	46	Good	Good	0.8
Example 3	20	52	Good	Good	0.8
Example 4	23	54	Good	Good	0.7
Example 5	25	51	Good	Good	0.7
Example 6	27	58	Good	Good	0.7
Example 7	31	64	Good	Good	0.8
Example 8	29	60	Good	Good	0.8
Example 9	17	44	Good	Good	0.8
Comparative Example 1	53	124	Good	Background Fogging Occurred	1.0
Comparative Example 2	48	106	Good	Background Fogging Occurred	1.3
Comparative Example 3	47	87	Good	Black Scratches Occurred	1.7

Table 2 (continued)

Embodiment No.	Potential Variation after 100,000 copies		Image Evaluation		Amount of Reduced Thickness
	|ΔVb|	|ΔVw|	Image Quality of First Copy	Image Quality of 100,000th Copy	
Comparative Example 4	53	94	Good	Background Fogging and Black Scratches Occurred	2.0
Comparative Example 5	51	98	Good	Background Fogging Occurred	2.2

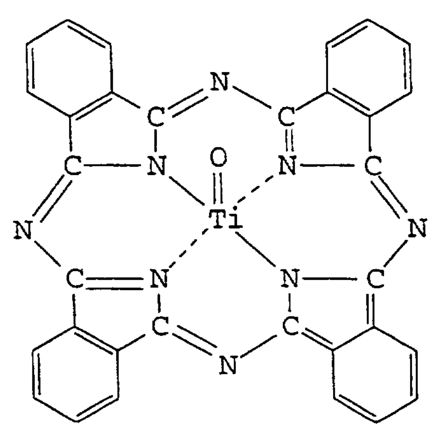
[0093] It is understood from Table 2 that in the Examples in which photoreceptors according to the present invention are used, there are observed less potential variations in both the solid black portion and the solid white portions and less amount of reduced thickness, and sharp images without background fogging and scratch troubles are obtainable. Whereas, in the comparative examples in which comparative photoreceptors were used, background fogging and scratch troubles were observed in the course of repeated image formation process, larger amount of reduced thickness observed, and images with good image quality cannot be obtained.

Example 10

<Preparation of Photoreceptor 10 according to the present invention>

[0094] On a cylindrical drum of 80 mmϕ made of aluminum, 0.3-µm-thick intermediate layer was formed by coating in the dip coating method a coating composition, prepared by dissolving 2 parts by weight of a modified-type polyamide resin " X-1874M", a product of Die Cell-Hurce Ltd., in a mixed solvent consisting of 90 parts by volume of methanol and 10 parts by volume of butanol. Next, 0.8 part by weight of a polyvinyl butyral resin "ESLEC BL-S", a product of Sekisui Chemical Industry Co., Ltd., was dissolved in 100 parts by weight of methylisopropyl ketone and to the thus obtained composition 20 parts by weight of cyclohexane, and to the thus prepared composition 2 parts by weight of CGM-2, of which chemical structure thereof is given below, was mixed and dispersed, to prepare a coating composition. This coating composition was coated on the above-mentioned intermediate layer by dip coating, and was dried, to form a 0.2-µm-thick charge generation layer.

Structure of CGM-2



[0095] Next, 120 parts by weight of a polycarbonate resin "EUPIRON Z300, a product of Mitsubishi Gas Chemical Co., Ltd., as a binder and 15 parts by weight of a charge transport material Compound (T-9) were dissolved and dispersed in 100 parts by volume of 1,2-dichloroethane, to prepare a coating composition. Then this coating composition was coated by dip coating method on the above-mentioned charge generation layer and was dried, to form a first charge transfer layer with dry layer thickness of 25 μm.

[0096] Then, another coating composition, in which 6 parts by weight of binder resin "Z-800, 2.54 parts by weight of silica particles (SO-C1) and 4 parts by weight of the charge transport material (T-9) were dissolved in 100 parts by weight of 1,2-dichloroethane, was coated using a ring-shaped coating amount regulation-type coating machine on the above-mentioned first charge transport layer, to form a 1-μm-thick second charge transport layer, thus to manufacture Photoreceptor-10 according to the present invention.

[0097] The photoreceptors for Example 10 were mounted one by one on the above-mentioned copying machine U-Bix 4145 and 100,000-time image formation test was carried out in the same manner as in Example 1, and image evaluation and measurements of the potential variation between the first copy and the 100,000th copy were conducted in the same manner as in Example 1. Results are shown in Table 3.

Table 3

Embodiment No.	Potential Variation after 100,000 copies		Image Evaluation		Amount of Remaining Solvent (%)
	|ΔVb|	|ΔVw|	Image Quality of First Copy	Image Quality of 100,000th Copy	
Example 10	37	55	Good	Good	0.19

[0098] In Example 10, again, superior results were obtained with respect to the photoreceptors according to the present invention.

Examples 11 through 18 and Comparative Examples 6 through 10.

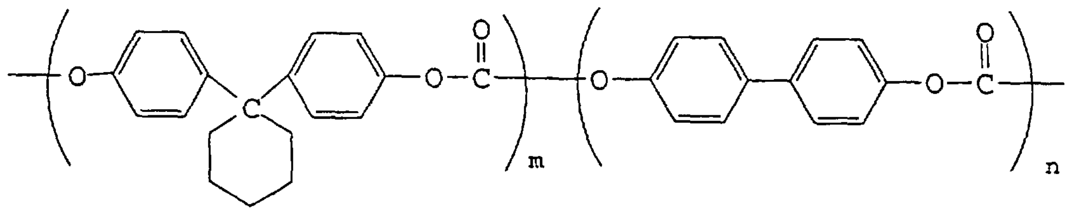
<Preparation of Photoreceptor-11 for Example 11 according to the present invention>

[0099] On a cylindrical drum of 80 mmϕ made of aluminum, an intermediate layer, a charge generation layer and a first charge transport layer were formed in the same manner as in Example 1. Then, 1.5 parts by weight of polycarbonate resin having a structure represented (B-1) given below as a binder and part by weight of a charge transport material (T-9) were dissolved and dispersed in 100 parts by volume of 1,2-dichloroethane and thus prepared coating composition was coated using a ring-shaped coating amount regulation-type coating machine, as illustrated in Fig. 3, on the above-mentioned first charge transport layer, dried at 110 °C for one hour, to form 3-μm-thick second charge transport layer. And, thus twelve photoreceptors for Example, as shown in Table 5, were obtained. The amount of the remaining solvent with respect to the total weight of the photosensitive layers including the intermediate layer was 0.41% by weight.

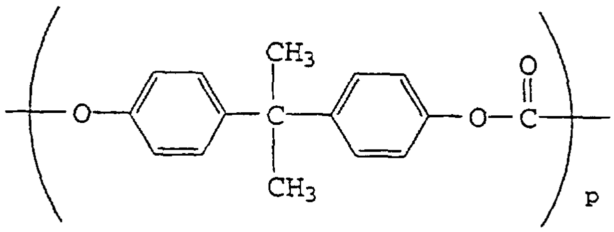
[0100] Preparation of Photoreceptors 12 through 18 according to the present invention and Comparative Photoreceptors 6 through 10.

[0101] Photoreceptor 12 through 18 and Comparative Photoreceptor 6 through 10 were manufactured in the same manner as Photoreceptor 11, provided that in these photoreceptors, binder in the second charge transfer material, molecular weight, layer thickness in Photoreceptor 11 were changed as shown in Table 4. Further in Comparative 9, the second CTL in Example 11 was not provided, and, instead . thickness of the first CTL was made to be 28 μm. The amount of the remaining solvent with respect to the respective photoreceptors are given in Table 4. Evaluation was made in the same manner as in Example 1. Results are shown in Table 5.

B-1



B-2



B-3

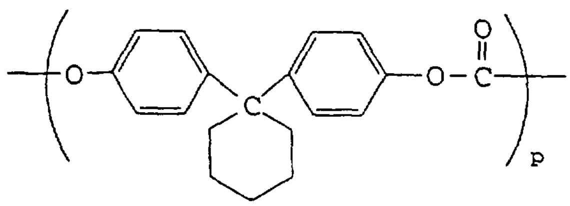


Table 4

Embodiment No.	Second Charge Transport Layer		Layer Thickness		Drying Temperature	Amount of Remaining Solvent (% by weight)
	Structure of Binder	Molecular Weight	Second CTL	First and Second CTL		
Example 11	B-1	250,000	3 μm	28 μm	110°C	0.41
Example 12	B-1	180,000	9 μm	34 μm	110°C	0.27
Example 13	B-1	120,000	5 μm	30 μm	110°C	0.20
Example 14	B-1	80,000	5 μm	30 μm	110°C	0.18
Example 15	B-2	200,000	5 μm	30 μm	110°C	0.35
Example 16	B-3	180,000	2 μm	27 μm	110°C	0.28
Example 17	B-3	120,000	5 μm	30 μm	110°C	0.22
Example 18	B-3	80,000	5 μm	30 μm	110°C	0.18

Table 4 (continued)

Embodiment No.	Second Charge Transport Layer		Layer Thickness		Drying Temperature	Amount of Remaining Solvent (% by weight)
	Structure of Binder	Molecular Weight	Second CTL	First and Second CTL		
Comparative example 6	B-1	30,000	5 μm	30 μm	110°C	0.20
Comparative example 7	B-2	30,000	5 μm	30 μm	110°C	0.22
Comparative example 8	B-3	30,000	5 μm	30 μm	110°C	0.22
Comparative example 9	Without Second CTL of Example 10; Thickness of First CTL: 28 μm			28 μm	110°C	0.18
Comparative example 10	Without First CTL of Example 10; Thickness of Second CTL: 28 μm			28 μm	110°C	1.02

Table 5

Embodiment No.	Potential Variation after 300,000 copies		Image Evaluation		Amount of Reduced Thickness
	$\|\Delta Vb\|$	$\|\Delta Vw\|$	Image Quality of First Copy	Image Quality of 300,000th Copy	
Example 11	22	54	Good	Good	2.2
Example 12	40	101	Good	Good	2.8
Example 13	28	88	Good	Good	3.4
Example 14	42	104	Good	Good	5.0
Example 15	30	75	Good	Good	3.1
Example 16	25	67	Good	Good	2.9
Example 17	33	84	Good	Good	3.5
Example 18	43	108	Good	Good	4.9
Comparative Example 6	56	139	Good	Black Scratches Occurred	11.2
Comparative Example 7	50	144	Good	Black Scratches Occurred	14.3
Comparative Example 8	59	123	Good	Black Scratches Occurred	11.7
Comparative Example 9	56	140	Good	Black Scratches Occurred	10.6
Comparative Example 10	64	172	Uneven Density Observed	Uneven Density, Black Scratches and Background Fogging Occurred	7.0

[0102] The result listed in Table 5 shows that photoreceptors according to the present invention show little potential change even after 300,000 copying operations, that images with excellent quality can be obtained and that abrasion of the layer is also little.

Examples 19 through 22

<Preparation of Photoreceptors 19 through 22>

[0103] On a cylindrical drum of 80 mmϕ made of aluminum, an intermediate layer, a charge generation layer and a first charge transport layer were formed in the same manner as in Example 1. However, in these examples, binder, molecular weight and layer thickness of the first charge transport layer were changed to those as shown in Table 6, thus to manufacture Photoreceptors-19 through 22. The amount of the remaining solvent with respect to the total weight of the photosensitive layers including the intermediate layer are shown in Table 6. Results of evaluation which was carried out in the same manner as Example 1 are shown in Table 7.

Table 6

Embodiment No.	First Charge Transport Layer		Layer Thickness		Amount of Remaining Solvent (% by weight)
	Structure of Binder	Molecular Weight	First CTL	First and Second CTL	
Example 19	B-1	20,000	30 µm	33 µm	0.35
Example 20	B-1	50,000	20 µm	23 µm	0.39
Example 21	B-3	10,000	30 µm	33 µm	0.40
Example 22	B-3	80,000	20 µm	23 µm	1.25

Table 7

Embodiment No.	Potential Variation after 300,000 copies		Image Evaluation		Amount of Reduced Thickness
	$\lvert\Delta Vb\rvert$	$\lvert\Delta Vw\rvert$	Image Quality of First Copy	Image Quality of 300,000th Copy	
Example 19	23	44	Good	Good	2.0
Example 20	27	53	Good	Good	2.2
Example 21	25	49	Good	Good	2.6
Example 22	40	95	Good	Good	3.7

[0104] Table 7 shows that photoreceptors according to the present invention show little potential change even after 300,000 copying operations, that images with excellent quality can be obtained and that abrasion of the layer is also little.

[0105] According to the present invention , it is possible to obtain a photoreceptor with enhanced durability without causing insufficient cleaning, a method of manufacturing the same, an electrophotographic apparatus and an apparatus unit used for the same, in which said photoreceptor is employed was obtained.

Claims

1. A photoreceptor for electro-photography comprising a photosensitive layer on an electro-conductive support, said photosensitive layer comprises a charge transport layer comprising a second charge transport layer which is an outermost surface layer of said photoreceptor and a first charge transport layer which is provided beneath said

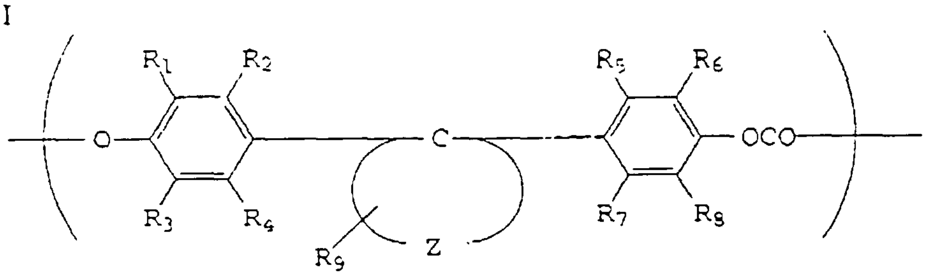
second charge transport layer, a carrier transport material being contained in each charge transport layer,

wherein said second charge transport layer comprises polycarbonate resin having second viscometric average molecular weight of at least 40,000 and said first charge transport layer comprises polycarbonate resin having first viscometric average molecular weight being not greater than said second viscometric average molecular weight, and

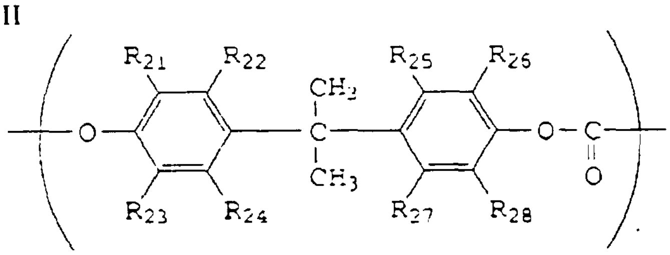
an amount of solvent remainblg in said photosensitive layer is not more than 2% by weight of said photosensitive layer.

2. The photoreceptor for electrophotography of Claim 1. wherein said polycarbonate resin comprises a structural unit represented by at least one of Formula 1 or Formula II

Formula I



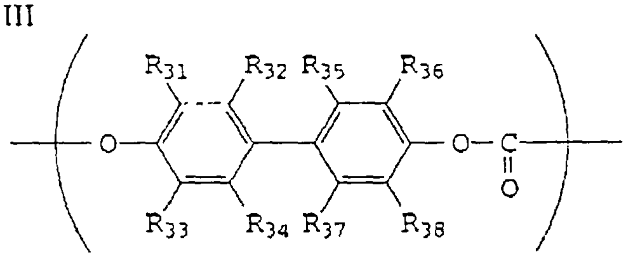
Formula II



wherein R_1 through R_8 and R_{21} through R_{28} independently represent hydrogen, halogen, an alkyl group, a cycloalkyl group and an aryl group, provided that these groups respectively have 1 to 10 carbon atoms and may be either substituted or unsubstituied, Z represents an atomic group forming a saturated or unsaturated carbon cycle having 4 to 11 carbon atoms. R_9 represents an alkyl group or an aryl group having 1 to 9 carbon atoms.

3. The photoreceptor for electro-photography of Claim 1, wherein the above-mentioned polycarbonate resin is a poly carbonate resin having a structural unit represented by formula III below:

Formula III



wherein R_{31} through R_{38} independently represent an atom or a group selected from a goup consisting of: a hy drogen atom, a halogen atom, an alky 1 group, a cycloalkyl group and an aryl group, provided that these groups respectively have 1 to 10 carbon atoms and they may be either substituted or unsubstituted.

4. The photoreceptor of Claim 1 wherein the second charge transport layer contains silica particles in amount of 1 to 200% by weight based on a binder in said second charge transport layer.

5. A photoreceptor for electrophotography of Claim 1, wherein the second viscometric average molecular weight is greater than 100,000.

6. The photoreceptor for electro-photogaphy of Claim 5, wherein the second viscometric average molecular weight is not grater than 500,000.

7. The photoreceptor for electro-photography of Claim 1, wherein the first viscometric average molecular weight is not greater than 50,000.

8. The photoreceptor for electrophotography of Claim 1. wherein the second charge transport layer comprises silica panicles, said silica particles having heat absorption energy change value DH controlled under condition at 80% relative humidity at temperature of 40° to 200°C which is 0 to 20 Joule/g; and a volume average particle diameter of said silica particles being 0.05 µm to 2 µm.

9. The photoreceptor for electrophotography of Claim I, wherein said first viscometric average molecular weight is 20,000 to 40,000.

10. The photoreceptor for electrophotography of Claim 1, wherein a thickness of the second charge transport layer is not more than 10 µm.

11. The photoreceptor for electrophotography of Claim 1, wherein a thickness of the charge transport layer is 5 to 50 µm.

12. The photoreceptor for electrophotography of Claim 11, wherein a thickness of the second charge transport layer is less than a thickness of the first charge transport layer.

Patentansprüche

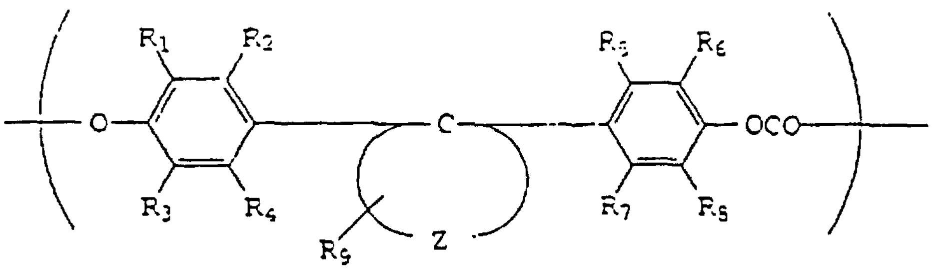
1. Photorezeptor für die Elektrophotographie, umfassend eine lichtempfindliche Schicht auf einem elektrisch leitenden Schichtträger, wobei die lichtempfindliche Schicht eine ladungtransportierende Schicht mit einer die äußerste Oberflächenschicht des Photorezeptor bildenden zweiten ladungtransportierenden Schicht und einer unter der zweiten ladungtransportierenden Schicht vorgesehenen ersten ladungtransportierenden Schicht umfasst, wobei in jeder ladungtransportierenden Schicht ein Ladungsträger transportierendes Material enthalten ist,

wobei die zweite ladungtransportierende Schicht ein Polycarbonatharz mit einem zweiten viskosimetrischen durchschnittlichen Molekulargewicht von mindestens 40000 und die erste ladungtransportierende Schicht ein Polycarbonatharz mit einem ersten viskosimetrischen durchschnittlichen Molekulargewicht, das nicht größer als das zweite viskosimetrische durchschnittliche Molekulargewicht ist, umfasst und

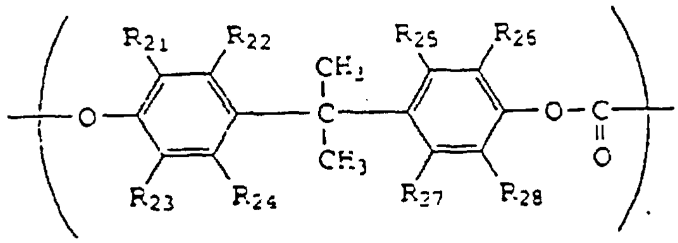
wobei die Menge an in der lichtempfindlichen Schicht verbliebenem Lösungsmittel nicht mehr als 2 Gew.-% der lichtempfindlichen Schicht beträgt.

2. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei das Polycarbonatharz eine Struktureinheit entsprechend mindestens einer der Formeln I oder II

Formel I



Formel II



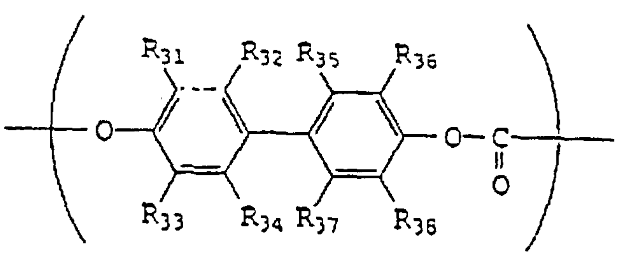
worin bedeuten:

R_1 bis R_8 und R_{21} bis R_{28} unabhängig voneinander Wasserstoff, Halogen, eine Alkylgruppe, eine Cycloalkylgruppe und eine Arylgruppe, wobei gilt, dass diese Gruppen jeweils 1-10 Kohlenstoffatome aufweisen und unsubstituiert oder substituiert sein können;
Z eine einen gesättigten oder ungesättigten Kohlenstoffring mit 4-11 Kohlenstoffatomen bildende Atomgruppe, und
R_9 eine Alkylgruppe oder eine Arylgruppe mit 1-9 Kohlenstoffatomen

umfasst.

3. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei das genannte Polycarbonatharz aus einem Polycarbonatharz mit einer Struktureinheit entsprechend der Formel III

Formel III



worin R_{31} bis R_{38} unabhängig voneinander für ein Atom oder eine Gruppe, ausgewählt aus der Gruppe, bestehend aus einem Wasserstoffatom, einem Halogenatom, einer Alkylgruppe, einer Cycloalkylgruppe und einer Arylgruppe, stehen, wobei gilt, dass diese Gruppen jeweils 1-10 Kohlenstoffatome aufweisen und entweder substituiert oder unsubstituiert sein können, besteht.

4. Photorezeptor nach Anspruch 1, wobei die zweite ladungtransportierende Schicht Siliciumdioxidteilchen in einer Menge von 1 bis 200 Gew.-%, bezogen auf ein in der zweiten ladungtransportierenden Schicht enthaltenes Bindemittel, enthält.

5. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei das zweite viskosimetrische durchschnittliche Molekulargewicht über 100000 liegt.

6. Photorezeptor für die Elektrophotographie nach Anspruch 5, wobei das zweite viskosimetrische durchschnittliche Molekulargewicht nicht größer als 500000 ist.

7. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei das erste viskosimetrische durchschnittliche Molekulargewicht nicht größer als 50000 ist.

8. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei die zweite ladungtransportierende Schicht Siliciumdioxidteilchen mit einem bei 80 % relativer Luftfeuchtigkeit und einer Temperatur von 40° bis 200 °C kontrollierten Wärmeabsorptionsenergieänderungs-Wert DH von 0-20 Joule/g und einem volumengemittelten Teilchendurchmesser von 0,05 bis 2 µm umfasst.

9. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei das erste viskosimetrische durchschnittliche Molekulargewicht 20000-40000 beträgt.

10. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei die Dicke der zweiten ladungtransportierenden Schicht nicht mehr als 10 µm beträgt.

11. Photorezeptor für die Elektrophotographie nach Anspruch 1, wobei die Dicke der ladungtransportierenden Schicht 5-50 µ m beträgt.

12. Photorezeptor für die Elektrophotographie nach Anspruch 11, wobei die Dicke der zweiten ladungtransportierenden Schicht geringer als die Dicke der ersten ladungtransportierenden Schicht ist.

Revendications

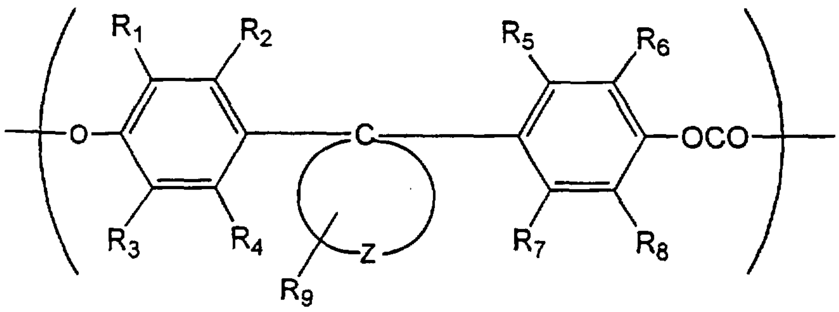
1. Photorécepteur pour électro-photographie comprenant une couche photosensible sur un support électro-conducteur, ladite couche photosensible comprenant une couche de transport de charges comprenant une seconde couche de transport de charges qui est une couche externe dudit photorécepteur et une première couche de transport de charges qui est prévue sous ladite seconde couche de transport de charges, un matériau de transport support étant contenu dans chaque couche de transport de charges,

caractérisé en ce que ladite seconde couche de transport de charges comprend une résine polycarbonate ayant une seconde masse moléculaire moyenne viscosimétrique d'au moins 40 000 et ladite première couche de transport de charges comprend une résine polycarbonate ayant une première masse moléculaire moyenne viscosimétrique qui n'est pas supérieure à ladite seconde masse moléculaire moyenne viscosimétrique, et

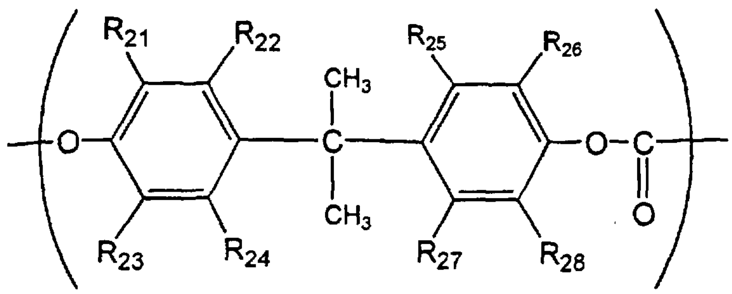
une quantité de solvant restant dans ladite couche photosensible n'étant pas supérieure à 2% en poids de ladite couche photosensible.

2. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que ladite résine polycarbonate comprend une unité structurelle représentée par au moins une des formule I ou formule II

Formule I

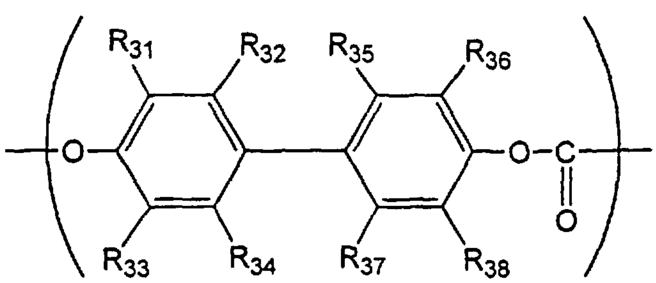


Formule II



formules dans lesquelles R_1 à R_8 et R_{21} à R_{28} représentent indépendamment l'hydrogène, un halogène, un groupe alkyle, un groupe cycloalkyle et un groupe aryle, sous réserve que ces groupes aient respectivement 1 à 10 atomes de carbone et puissent être substitués ou non substitués ; Z représente un groupe atomique formant un cycle carboné saturé ou insaturé ayant 4 à 11 atomes de carbone, R_9 représente un groupe alkyle ou un groupe aryle ayant 1 à 9 atomes.

3. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que la résine polycarbonate mentionnée ci-dessus est une résine polycarbonate ayant une unité structurelle représentée par la formule III ci-dessous :



dans laquelle R_{31} à R_{38} représentent indépendamment un atome ou un groupe choisi dans le groupe constitué par un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe cycloalkyle et un groupe aryle, sous réserve que ces groupes aient respectivement 1 à 10 atomes de carbone et qu'ils puissent être substitués ou non substitués.

4. Photorécepteur selon la revendication 1, caractérisé en ce que la seconde couche de transport de charges contient des particules de silice en une quantité de 1 à 200% en poids rapporté à un liant dans ladite seconde couche de transport de charges.

5. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que la seconde masse moléculaire moyenne viscosimétrique est supérieure à 100 000.

6. Photorécepteur pour électro-photographie selon la revendication 5, caractérisé en ce que la seconde masse moléculaire moyenne viscosimétrique est supérieure à 500 000.

7. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que la seconde masse moléculaire moyenne viscosimétrique est supérieure à 50 000.

8. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que la seconde couche de transport de charges comprend des particules de silice, lesdites particules de silice ayant une valeur de changement d'énergie d'absorption de chaleur DH contrôlée dans un état de 80% d'humidité relative à une température de 40°C à 200°C qui est égale à 20 Joules/g ; et un diamètre moyen de particules en volume desdites particules de silice étant de 0,05 μm à 2 μm.

9. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que ladite première masse moléculaire moyenne viscosimétrique est de 20 000 à 40 000.

10. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que l'épaisseur de la seconde couche de transport de charges n'est pas supérieure à 10 μm.

11. Photorécepteur pour électro-photographie selon la revendication 1, caractérisé en ce que l'épaisseur de la couche de transport de charges est de 5 à 50 μm.

12. Photorécepteur pour électro-photographie selon la revendication 11, caractérisé en ce que l'épaisseur de la seconde couche de transport de charges est inférieure à l'épaisseur de la première couche de transport de charges.

FIG. 1 (A)

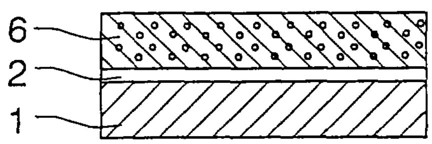


FIG. 1 (D)

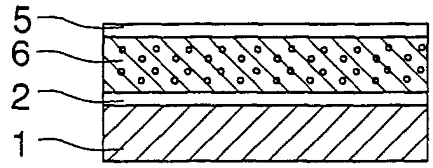


FIG. 1 (B)

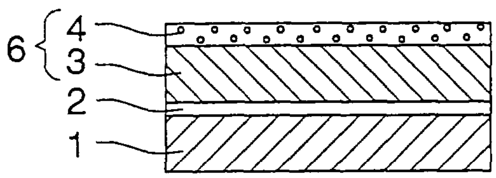


FIG. 1 (E)

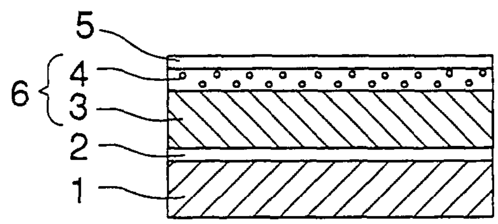


FIG. 1 (C)

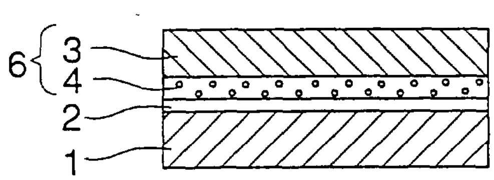


FIG. 1 (F)

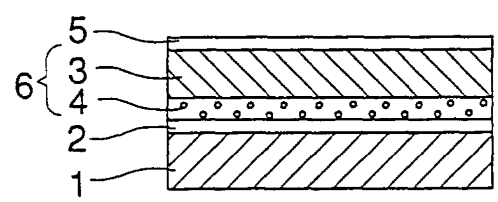


FIG. 2

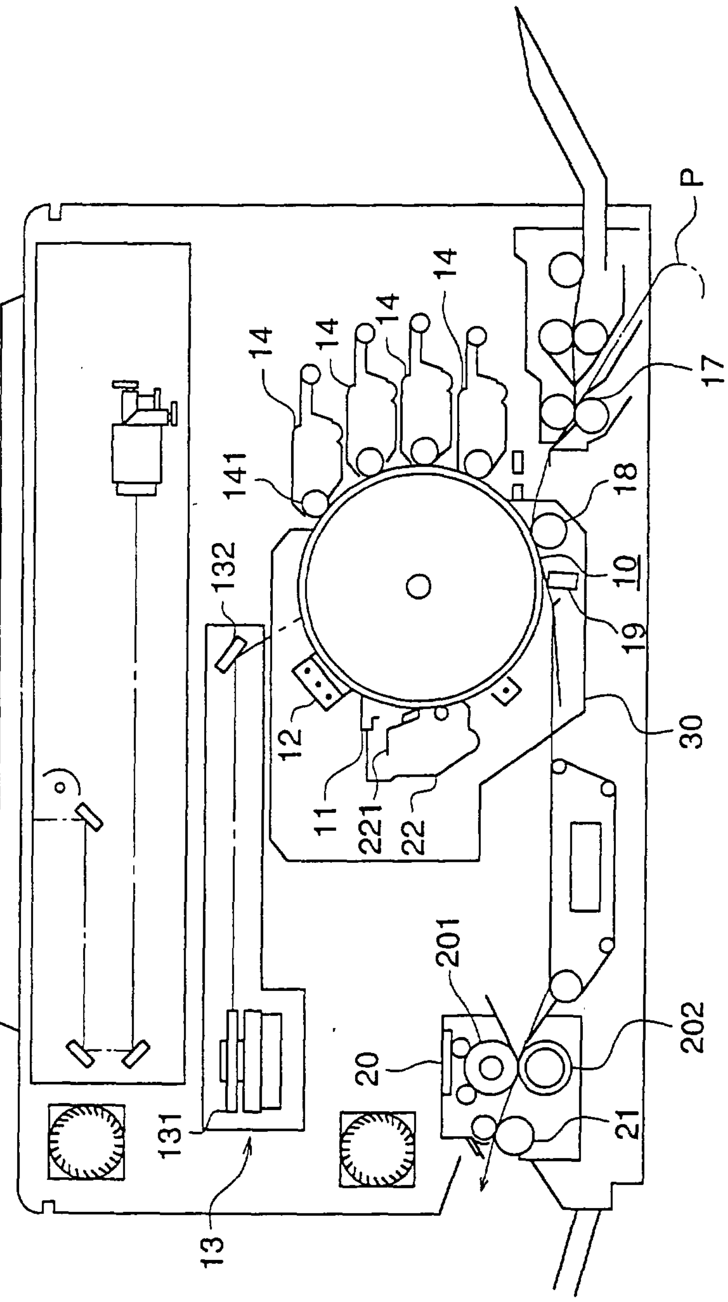


FIG. 3

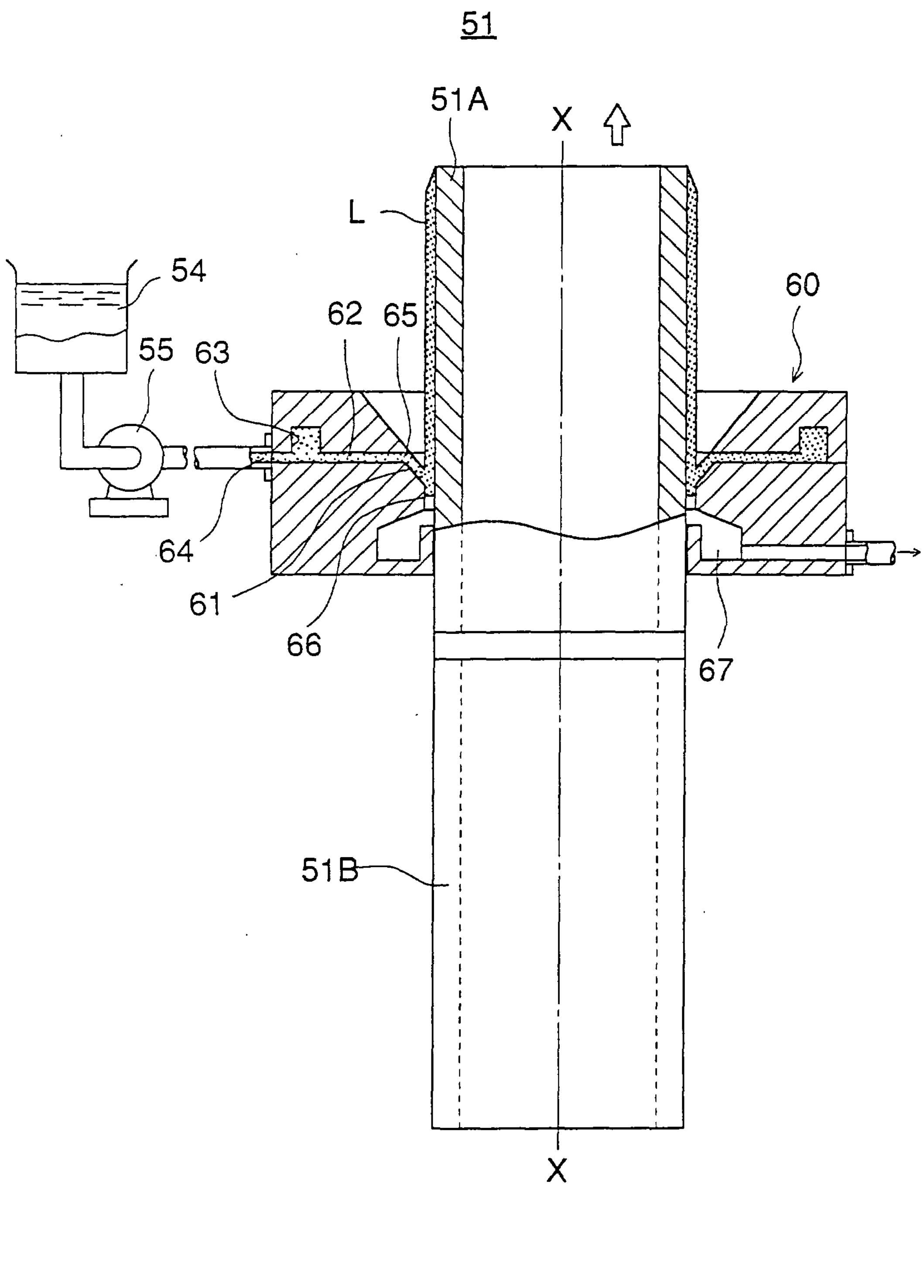


FIG. 4