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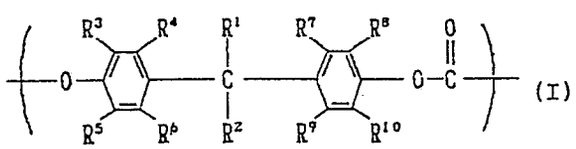
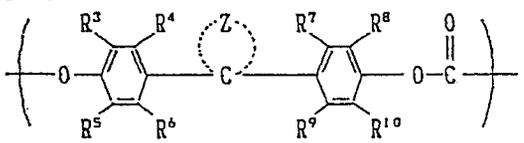
## (54) Photoreceptor.

(57) Photoreceptor comprising an electroconductive base that has a carrier generation layer formed thereon which is overlaid with a carrier transport layer. This photoreceptor is characterized in that said carrier transport layer comprises at least two constituent layers, that the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is closer to said electroconductive base is higher than the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is more remote from said electroconductive base, and that the binder in the outermost constituent layer of said carrier transport layer contains a polycarbonate having as the principal recurring unit a structural unit represented by the following general formula (I) and/or a structural unit represented by the following general formula (II):



(I)

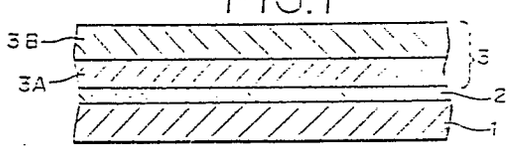
(where $R^1$ and $R^2$ each is a hydrogen atom, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted carbocyclic group, or a substituted or unsubstituted aromatic group, provided that at least one of $R^1$ and $R^2$ is a "bulky" group; and $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is a hydrogen atom, a halogen atom, a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted carbocyclic group);



(II)

where $R^3$, $R^4$ $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is same as defined above; Z is the atomic group necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring).

FIG. 1

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**Description**

# PHOTORECEPTOR

## BACKGROUND OF THE INVENTION

The present invention relates to a photoreceptor such as one to be used in electrophotography.

In electrophotographic copying by the Carlson process, an electric charge layer is deposited on the surface of a photoreceptor and after exposure to form a latent electrostatic image, it is developed by a toner and the resulting visible image is transferred and fixed to a receiving sheet such as paper. Subsequently, the toner is removed from the surface of the photoreceptor and any residual charges are neutralized to erase the electrostatic image completely and condition the photoreceptor for another cycle, thereby enabling its cyclic use for a prolonged period.

For successful operation of electrophotography, the photoreceptor must satisfy various requirements not only in terms of electrophotographic characteristics such as good chargeability and sensitivity plus small dark decay but also in terms of physical properties such as long run length and high resistance to wear and moisture during cyclic use, as well as in terms of resistance to environmental conditions such as ozone generated upon corona discharging and ultraviolet radiation emitted during exposure.

Electrophotographic photoreceptors that have been commonly used in the art are inorganic products having a photosensitive layer that is based on inorganic photoconductive materials such as selenium, zinc oxide and cadmium sulfide. The use of various organic photoconductive materials as the effective component of light-sensitive layers in electrophotographic photoreceptors has been the subject of active research and development efforts in the recent years. For example, an organic photoreceptor having a light-sensitive layer containing poly-N-vinylcarbazole and 2,4,7-trinitro-9-fluorenone has been described in JP-B-50-10496 (the term "JP-B" as used hereunder means an "examined Japanese patent publication"). However, this photoreceptor is not completely satisfactory in terms of sensitivity and durability. In order to overcome this problem, attempts have been made to develop an organic photoreceptor of high sensitivity and durability by composing the light-sensitive layer of two different materials, one being responsible for carrier generation and the other for carrier transport. Electrophotographic photoreceptors of this "functionally separated type" provide for a great latitude in the selection of appropriate materials that exhibit the intended functions, and this enables photoreceptors having desired characteristics to be prepared fairly easily.

The organic electrophotographic photoreceptors described above have the advantage that the light-sensitive layer can be formed by coating techniques, so not only can they be manufactured at low cost without causing environmental pollution but they can also be fabricated in various forms including sheet. On the other hand, conventional organic electrophotographic photoreceptors have had the following problems that demand solution.

(1) The light-sensitive layer is formed of a low-molecular weight organic compound dispersed in a high-molecular weight organic binder resin, so that the mechanical strength of the layer is not high enough to prevent the photoreceptor's surface from being damaged or wearing by abrasion with the developing blade or some other phenomena that will occur during cyclic use of the photoreceptor.

(2) The photoreceptor is principally to be used as a negatively chargeable type and as shown in JP-A-60-247647 (the term "JP-A" as used hereunder means an "unexamined published Japanese patent application"), it is composed of a base that is overlaid with a thin carrier generation layer which in turn is overlaid with a comparatively thick carrier transport layer. When it is to be used as a negatively chargeable type, the photoreceptor has a large carrier (hole) mobility and permits the use of hole transporting materials, which is a definite advantage in such aspects as photosensitivity. In contrast, electron transporting materials available today very rarely have desirable characteristics or they are unsuitable for practical use because of their potential carcinogenic or teratogenic nature.

A problem with the negatively chargeable photoreceptor is that negative corona discharging will generate an undesirably larger volume of ozone into the operating atmosphere during negative charging with a charging device than in the case of positive corona discharge, with consequent deterioration of the environmental condition. This causes either adsorption of ionic species onto the surface of the photoreceptor or deterioration of the material in its surface and the resulting decrease in potential during cyclic use will lead to various undesired phenomena such as increased residual potential, lowered sensitivity and deteriorated image quality, thereby reducing the service life of the photoreceptor.

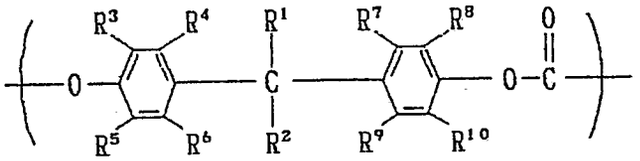
(3) Electrophotographic copiers are to be used under various conditions for an extended period and are often placed under hot and humid conditions. It is therefore necessary to develop a practical photoreceptor that has high resistance to the environment.

## SUMMARY OF THE INVENTION

An object, therefore, of the present invention is to provide a photoreceptor that has high mechanical

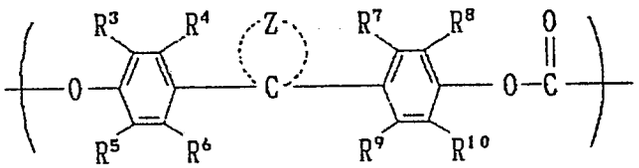
strength and good charging potential and sensitivity characteristics, that will not experience a substantial increase in residual potential, and that exhibits high resistance to the environment.

This object of the present invention can be attained by a photoreceptor comprising an electroconductive base that has a carrier generation layer formed thereon which is overlaid with a carrier transport layer, the improvement wherein said carrier transport layer comprises at least two constituent layers, the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is closer to said electroconductive base is higher than the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is more remote from said electroconductive base, and the binder in the outermost constituent layer of said carrier transport layer contains a polycarbonate having as the principal recurring unit a structural unit represented by the following general formula (I) and/or a structural unit represented by the following general formula (II):



( I )

(where $R^1$ and $R^2$ each is a hydrogen atom, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted carbocyclic group, or a substituted or unsubstituted aromatic group, provided that at least one of $R^1$ and $R^2$ is a "bulky" group; and $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is a hydrogen atom, a halogen atom, a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted carbocyclic group);



( II )

(where $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is same as defined above; Z is the atomic group necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring).

## BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 - 4 are partial cross sections showing different constructions of the electrophotographic photoreceptor of the present invention; and

Fig. 5 is a table showing the electrophotographic characteristics of the photoreceptor samples prepared in Examples 1 - 8 and Comparative Examples 1 - 6.

One of the major features of the photoreceptor of the present invention is that the carrier transport layer is divided into two or more constituent layers having different concentrations of carrier transport material. A constituent layer which is closer to said electroconductive base has a higher concentration of carrier transport material so that photocarriers generated in the carrier generation layer will be injected efficiently into the carrier transport layer. On the other hand, a constituent layer which is more remote from said electroconductive base has a lower concentration of carrier transport material, so that the reduced use of the carrier transport material having a low molecular weight will contribute to a corresponding increase in the mechanical strength of the carrier transport layer.

Another important feature of the present invention is that a polycarbonate having a structural unit represented by the general formula (I) and/or the general formula (II) as the principal recurring unit is incorporated as a binder in a constituent layer of said carrier transport layer which is the remotest from the electroconductive base. Polycarbonates having a structural unit represented by the general formula (I) and/or the general formula (II) as the principal recurring unit have high mechanical strength, good resistance to scratch and wear, long run length and desired charging performance. In particular, such polycarbonates have a hard surface while providing a reasonable degree of lubricity. They also have a high degree of transparency and insulating property and are highly miscible with the carrier transport material. In the polycarbonate, $R^1$ and $R^2$ at least one of which is "bulky" are bound to the central carbon atom of the bisphenol A portion or a ring is formed of Z around said carbon atom, so that said $R^1$ and/or $R^2$ or Z effectively prevents the molecular chain of the polycarbonate to be oriented in a certain direction. Hence, the polycarbonate will not crystallize to bleed out on the surface of the photosensitive layer being formed and deterioration of characteristics such as yield loss due to abnormal projections and defective image due to toner filming, or premature gelation of the coating solution can be prevented.

Further, the polycarbonates of the general formula (I) and the general formula (II) are impermeable to ozone and will hence reduce the chance of deterioration of the carrier transport material. This advantage is particularly notable in the photoreceptor of the present invention since a constituent layer of the carrier

transport layer which is more remote from the electroconductive base has a lower concentration of carrier transport material.

The carrier transport layer may be composed of two or three or more constituent layers. If it is made of three or more constituent layers, the content of carrier transport material is the highest in the constituent layer which is the closest to the electroconductive base, with said concentration being decreased toward the outer surface of the carrier transport layer.

Four basic compositions of the photoreceptor of the present invention are shown schematically in Figs. 1 - 4 for illustrative purposes.

The photoreceptor shown in Fig. 1 comprises an electroconductive base 1 overlaid with a carrier generation layer 2 that in turn is overlaid with a carrier transport layer 3 which is composed of constituent layers 3A and 3B. The electroconductive base 1 of the photoreceptor shown in Fig. 2 is formed of a flexible substrate 1A overlaid with an electroconductive layer 1B. In the photoreceptor shown in Fig. 3, the carrier generation layer 2 is overlaid with the carrier transport layer 3 composed of three constituent layers 3A, 3B and 3C. The photoreceptor shown in Fig. 4 is the same as that shown in Fig. 1 except that an intermediate layer or subbing layer 6 is provided between the carrier generation layer 2 and the electroconductive base 1.

The weight ratio of the content of the carrier transport material to binder material in a constituent layer of said carrier transport layer which is the remotest from the electroconductive base (hereinafter referred to as a outermost constituent layer of the carrier transport layer) (layer 38 in the examples shown in Figs. 1, 2 and 4, and layer 3C in the example shown in Fig. 3) is preferably not higher than 70 wt%, more preferably in the range of 5 - 70 wt%. If the weight ratio of the content of carrier transport material to binder material is adjusted to lie within this range, the strength of the carrier transport layer can be increased without sacrificing its ability to transport carriers.

The weight ratio of the content of carrier transport material to binder material in a constituent layer which is the closest to the electroconductive base (layer 3A in the examples shown in Figs. 1 - 4) is preferably at least 30 wt%, more preferably in the range of 30 - 300 wt%. If the weight ratio of the content of carrier transport material to binder material is adjusted to lie within this range, an increased amount of photocarriers can be injected into the carrier transport layer from the carrier generation layer. It is particularly noteworthy that the content of carrier transport material in this constituent layer can be increased to as high as 300 wt% and this has become possible for two reasons: first, the carrier transport layer is composed of two or more constituent layers, and second, the constituent layer the remotest from the electroconductive base has an increased strength.

The weight ratio of the content of carrier transport. material to binder material in a constituent layer which is the remotest from the electroconductive base preferably differs by at least 1.0 wt% from the weight ratio of the content of carrier transport material to binder material in a constituent layer which is the closest to the electroconductive base.

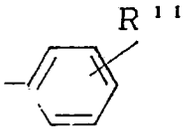
The binder in each of the constituent layers of the carrier transport layer may be made of a polycarbonate represented by the general formula (I) and/or the general formula (II). This is effective in achieving further increase in the strength of the carrier transport layer.

The materials of which the photoreceptor of the present invention are composed and their recipes are described below. First to be discussed is the polycarbonate having a structural unit represented by the general formula (I) and/or the general formula (II) as the principal recurring unit. Prevention of crystallization of the polycarbonate and the attendant advantages already described can be accomplished on account of the "bulkiness" of $R^1$ and $R^2$ in formula (I) or by the action of the ring formed of Z in formula (II). In connection with this, it is more preferred that $R^1$ and $R^2$ in formula (I) are different from each other or that they are bound asymmetrically if they are of the same group.

It is essential with the polycarbonate of formula (I) that at least one of $R^1$ and $R^2$ be a bulky group, preferably having at least 3 carbon atoms, in order to provide steric hindrance in such a way as to prevent orientation of the molecular chain.

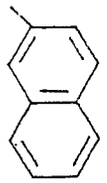
Illustrative examples of such "bulky" group are listed below:

(1)




where $R^{11}$ is a hydrogen atom, an alkyl group such as methyl, or an alkyl ester group represented by $+CH_2)_m COOR$ (where R is an alkyl group, and $m \geqq 1$);

(2)



(3) an alkyl group represented by $-C_mH_{2m+1}$ ($m \geqq 4$); and

(4) an alkyl ester group represented by $+CH_2)_m COOR^{12}$ (where $R^{12}$ is an alkyl group, and $m \geqq 2$).

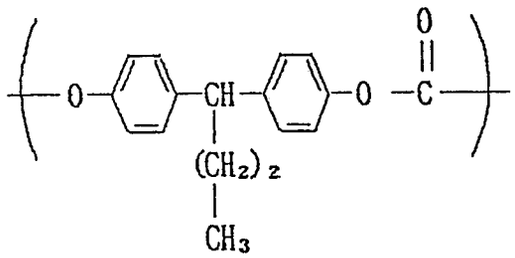
When either one of $R^1$ and $R^2$ is a bulky group, the other may be a hydrogen atom or an alkyl group such as methyl.

In the general formulas (I) and (II), $R^3$ - $R^{10}$ may represent not only a hydrogen atom but also a halogen atom such as Cl, Br or F, an alkyl group such as methyl, and a carbocyclic group such as cyclohexyl.

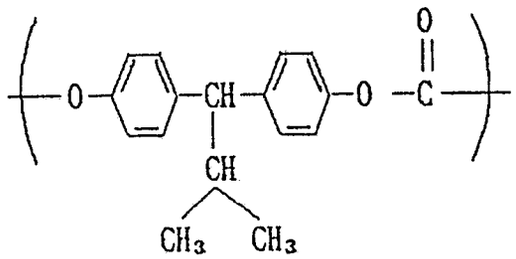
With the polycarbonate represented by the general formula (II), Z may be an atomic group that forms a 5- or 6-membered carbon ring or heterocyclic ring, such as a cyclohexyl group or a cyclopentyl group. These groups may be partly substituted by acetyl, acetylamino or other groups.

Illustrative examples of the structural units represented by general formulas (I) and (II) are listed below:

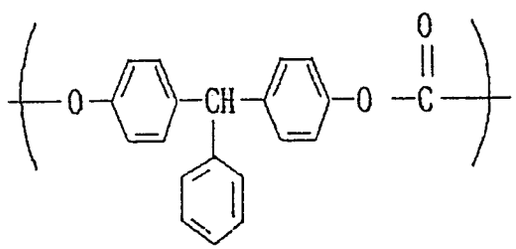
(I-1)



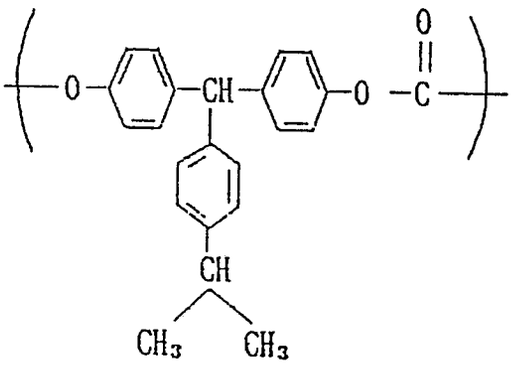
(I-2)



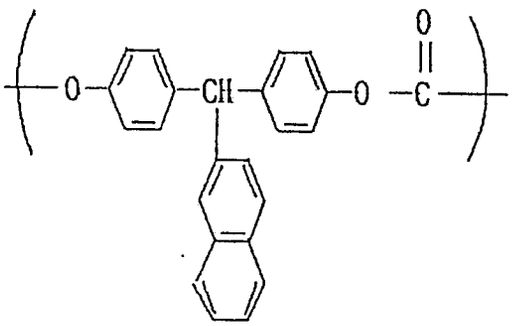
(I-3)



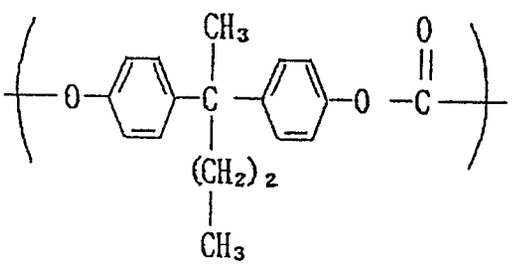
(I－4)



(I－5)



(I－6)



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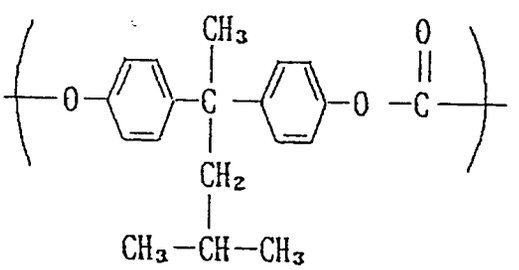
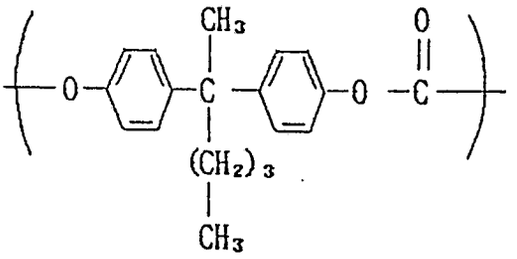


(I－8)



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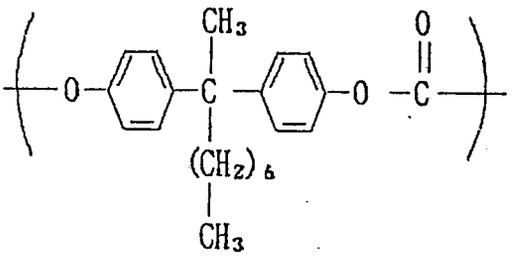

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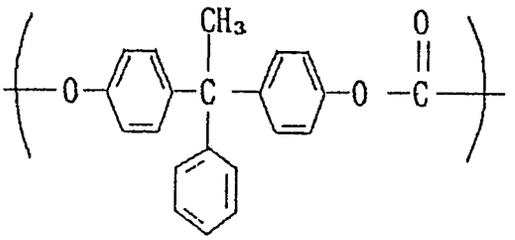
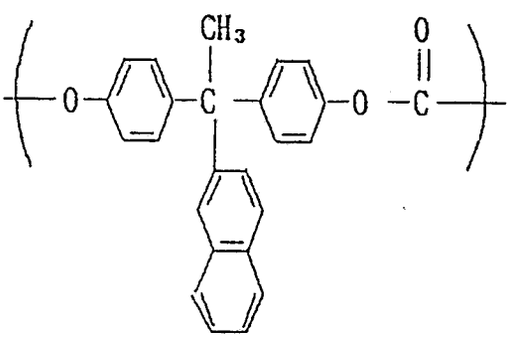


(I－11)



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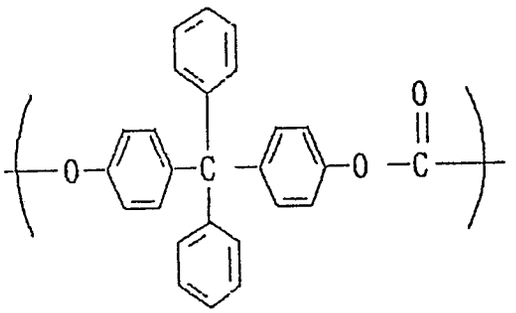

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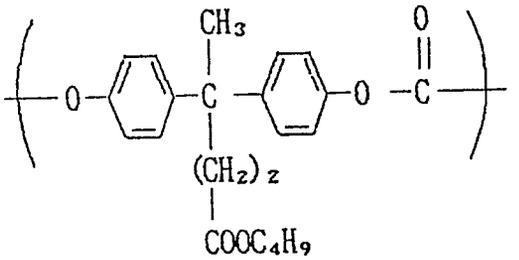

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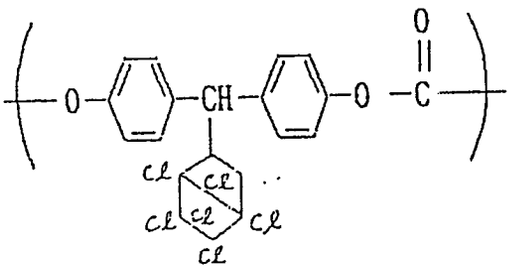
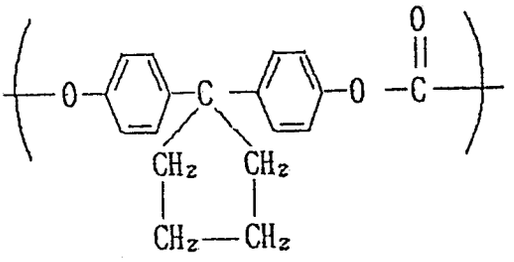
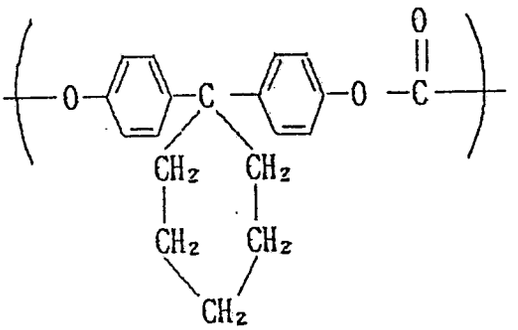


(Ⅱ－1)



(Ⅱ－2)



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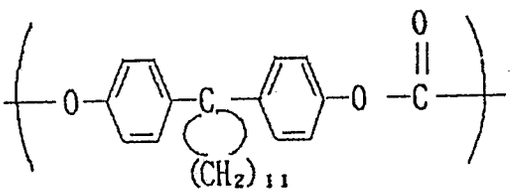

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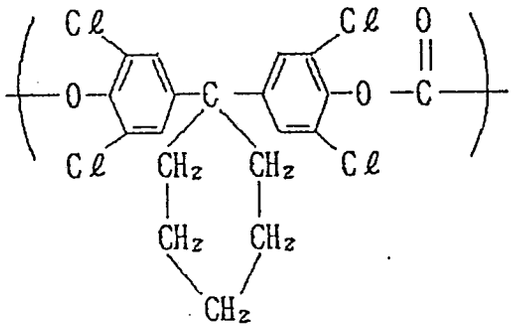

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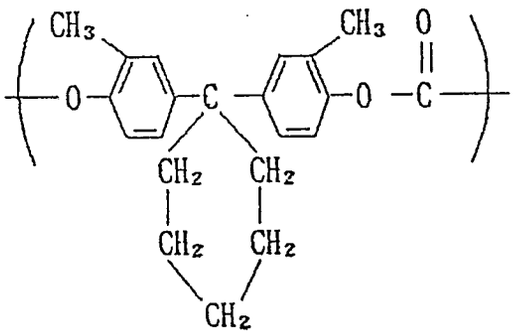

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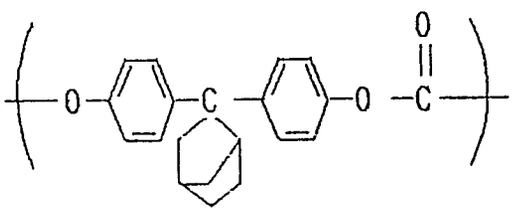
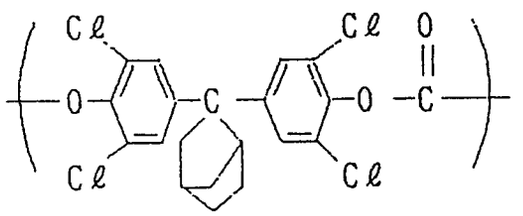
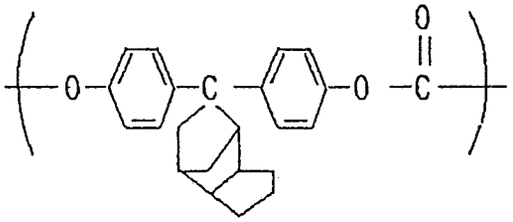


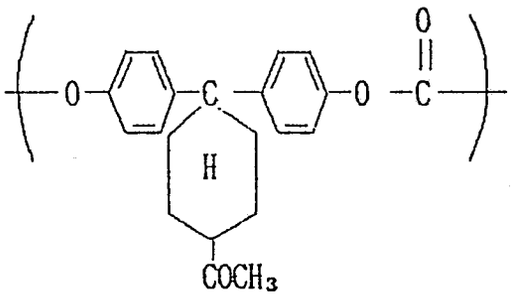
(Ⅱ－7)



(II－8)

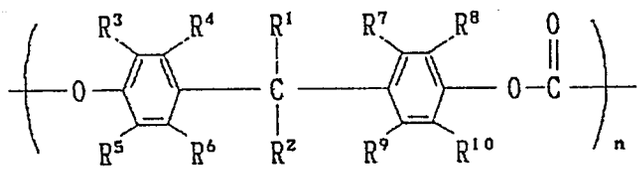


(II－9)



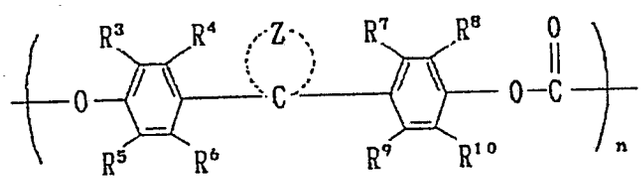
The polycarbonates that can be used in the present invention have as the principal recurring unit the structural unit represented by the general formula (I) and/or the structural unit represented by the general formula (II). The principal recurring unit may be a single structural unit represented by general formula (I) or general formula (II) (for example, the structural unit (I-2) may be the sole recurring unit), or two or more structural units represented by general formula (I) and/or general formula (II) may be co-condensed. If necessary, a recurring unit represented by general formula (I) and/or general formula (II) may be co-condensed with minor amounts of different other recurring units with a view to providing improved physical, chemical and electrical characteristics. The resulting polycarbonates of co-condensation type are included within the scope of the present invention as long as they are not detrimental to the purposes of the present invention. Specific examples of such polycarbonates of co-condensation type include a polycarbonate prepared by co-condensing 4,4′-dihydroxyphenyl-1,1-cyclohexane with a minor proportion of bisphenol A, and the product of polycondensation of 4,4′-dihydroxyphenyl-1,1-cyclohexane and an aromatic dicarboxylic acid such as terephthalic acid or isophthalic acid.

Additional examples of polycarbonates that can be used in the present invention are represented by the following general formulas (Ia) and (IIa):



( Ia )

where $R^1$, $R^2$, $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is same as defined for formulas (I) and (II); n is 10 - 5000, preferably 50 - 2000;



( IIa )

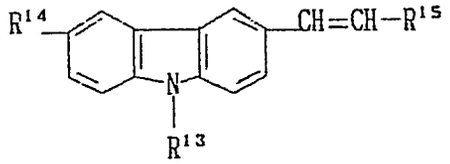
and where $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$, $R^{10}$, Z and n each is same as defined for general formulas (I) and (II).

The polycarbonate having the structural unit represented by general formula (II) as the principal recurring unit is preferred since it is capable of attaining the objects of the present invention in a more effective way. Particularly advantageous structural units are those identified above by (II-2), (II-4) and (II-9) which have a

cyclohexane ring bound to the central carbon atom of the bisphenol A portion, and the structural unit identified by (II-2) is most preferred.

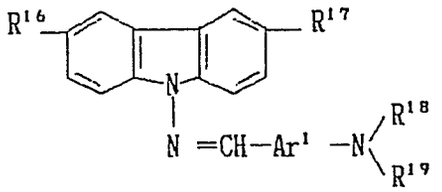
The carrier transport material to be incorporated in the carrier transport layer is described below.

Illustrative carrier transport materials include carbazole derivatives represented by the following general formula (III) and hydrazone compounds represented by the following general formulas (IV) - (VI):



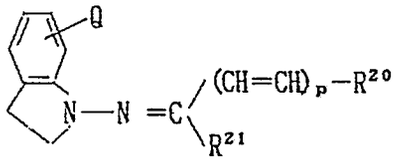
( III )

(where $R^{13}$ is a substituted or unsubstituted aryl group; $R^{14}$ is a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an alkoxy group, an amino group, a hydroxyl group or a substituted amino group; and $R^{15}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group);



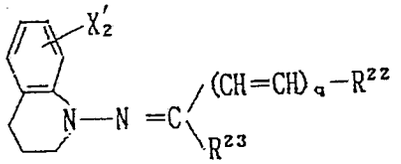
( IV )

(where $R^{16}$ and $R^{17}$ each is a hydrogen atom or a halogen atom; $R^{18}$ and $R^{19}$ each is a substituted or unsubstituted aryl group; and $Ar^1$ is a substituted or unsubstituted arylene group);



( V )

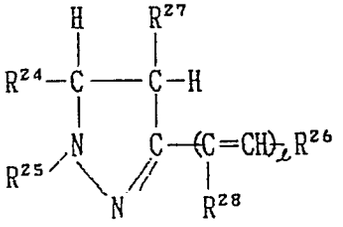
(where $R^{20}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; $R^{21}$ is a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; Q is a hydrogen atom, a halogen atom, an alkyl group, a substituted amino group, an alkoxy group or a cyano group; and p is an integer of 0 or 1);



( VI )

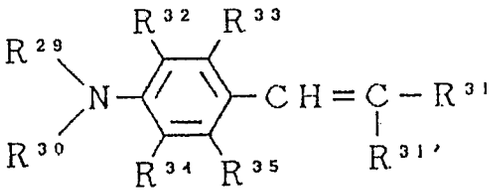
(where $R^{22}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; $R^{23}$ is a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; $X'_2$ is a hydrogen atom, a halogen atom, an alkyl group, a substituted amino group, an alkoxy group or a cyano group; and q is an integer of 0 or 1).

Carrier transport materials represented by the following general formulas (VII) - (IX) can also be used in the present invention:



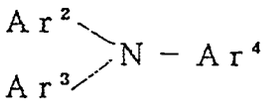
( VII )

(where $\ell$ is an integer of 0 or 1; $R^{24}$, $R^{25}$ and $R^{26}$ each is a substituted or unsubstituted aryl group; $R^{27}$ and $R^{28}$ each is a hydrogen atom, an alkyl group having 1 - 4 carbon atoms, a substituted or unsubstituted aryl or aralkyl group, provided that $R^{27}$ and $R^{28}$ are not a hydrogen atom at the same time, and when $\ell$ is 0, $R^{27}$ is not a hydrogen atom);



( VIII )

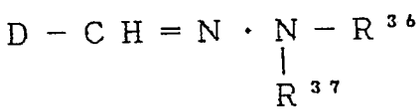
(where $R^{29}$ and $R^{30}$ is a substituted or unsubstituted alkyl or phenyl group, with the substituent being an alkyl, alkoxy or phenyl group; $R^{31}$ is a substituted or unsubstituted phenyl, naphthyl, anthryl, fluorenyl or heterocyclic group, with the substituent being an alkyl group, an alkoxy group, a halogen atom, a hydroxyl group or a phenyl group; $R^{13'}$ is a hydrogen atom, a substituted or unsubstituted alkyl or phenyl group; and $R^{32}$, $R^{33}$, $R^{34}$ and $R^{35}$ each is a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group or an alkylamino group);



( IX )

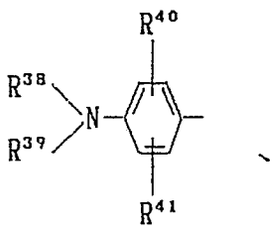
(where $Ar^2$ and $Ar^3$ each is a substituted or unsubstituted phenyl group, with the substituent being a halogen atom, an alkyl group, a nitro group or an alkoxy group; and $Ar^4$ is a substituted or unsubstituted phenyl, naphthyl, anthryl, fluorenyl or heterocyclic group, with the substituent being an alkyl group, an alkoxy group, a halogen atom, a hydroxyl group, an aryloxy group, an aryl group, an amino group, a nitro group, a piperidino group, a morpholino group, a naphthyl group, an anthryl group or a substituted amino group, provided that the last-mentioned substituted amino group has an acyl, alkyl, aryl or aralkyl group as the substituent).

Hydrazone compounds represented by the following general formula (X) may also be used in the present invention:



( X )

(where D is a substituted or unsubstituted phenyl group, or a substituted or unsubstituted carbazolyl group, as specifically illustrated by



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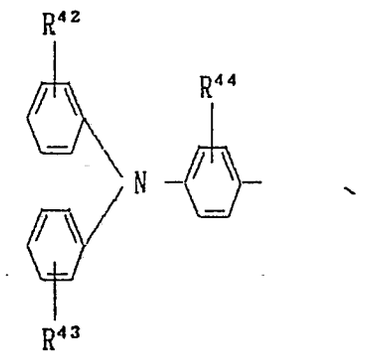

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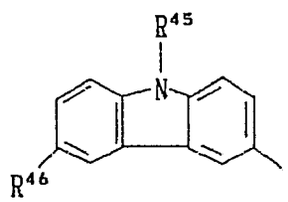


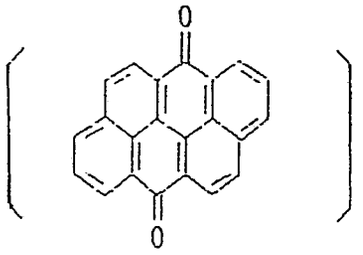
;

$R^{36}$ and $R^{37}$ each represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, or a substituted or unsubstituted aryl group (illustrative alkyl groups include methyl, ethyl, propyl and butyl; illustrative aralkyl groups include benzyl and phenethyl; illustrative aryl groups include phenyl, α-naphthyl and β-naphthyl; illustrative substituents include a halogen atom, an alkyl group, an alkoxy group and a substituted amino group such as dimethylamino, diethylamino, dipropylamino or dibenzylamino); $R^{38}$, $R^{39}$ and $R^{45}$ each represents the same as $R^{36}$ and $R^{37}$; and $R^{40}$, $R^{41}$, $R^{42}$, $R^{43}$, $R^{44}$ and $R^{46}$ each represents an alkyl group, an alkoxy group, a halogen atom, etc.)

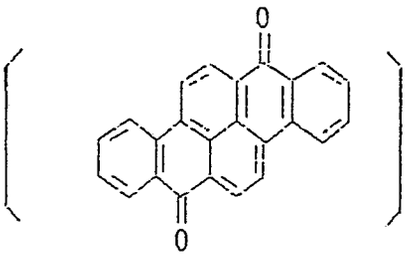
The carrier transport materials described above may be synthesized by known methods, one of which

comprises performing dehydrative condensation between α, β- unsaturated ketone and phenylhydrazine in the presence of an acid catalyst.

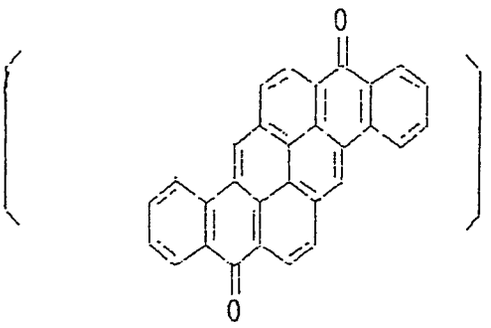
The carrier generation layer (CGL) in the photoreceptor of the present invention contains a carrier generation material (CGM) and polycyclic quinone pigments represented by the following general formulas (XI), (XII) and (XIII) may be used as CGM:



( XI )



( XII )

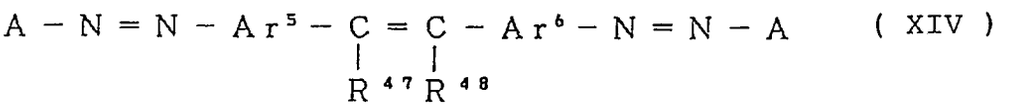


( XIII )

In each of these formulas, X is a halogen atom, a nitro group, a cyano group, an acyl group or a carboxyl group; n is an integer of 0 to 4; and m is an integer of 0 to 6.

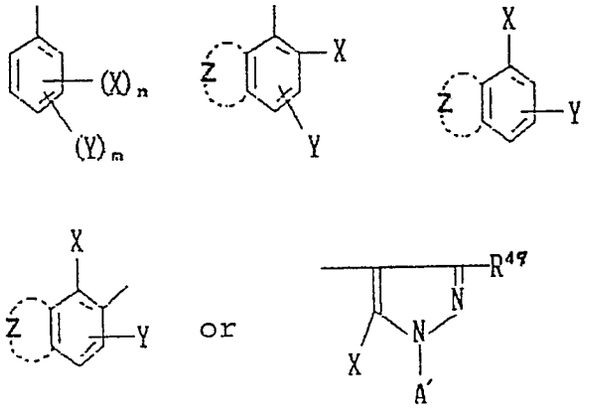
These polycyclic quinone pigments can be synthesized by known methods.

Other examples of useful CGM include bisazo compounds represented by the following general formula (XIV):

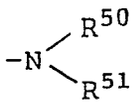


( XIV )

where $Ar^5$ and $Ar^6$ each is a substituted or unsubstituted carbocyclic aromatic group, or a substituted or unsubstituted heterocyclic aromatic group; $R^{47}$ and $R^{48}$ each is an electron withdrawing group or a hydrogen atom (at least one of $R^{47}$ and $R^{48}$ is -CN, a halogen such as -Cl or an electron withdrawing group such as $-NO_2$); and A is

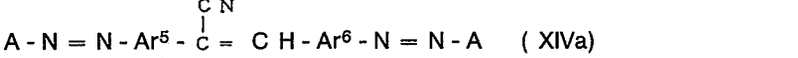


(X is a hydroxyl group,



or -$NHSO_2$-$R^{52}$ (where $R^{50}$, and $R^{51}$ each is a hydrogen atom or a substituted or unsubstituted alkyl group; $R^{52}$ is a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group); Y is a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an alkoxy group, a carboxyl group, a sulfo group, a substituted or unsubstituted carbamoyl group, or a substituted or unsubstituted sulfamoyl group (provided that Y may assume different groups when m is 2 or more); Z is the atomic group necessary to form a substituted or unsubstituted carbocyclic aromatic ring or a substituted or unsubstituted heterocyclic aromatic ring; $R^{49}$ is a hydrogen atom, a substituted or unsubstituted amino group, a substituted or unsubstituted carbamoyl group, a carboxyl group or an ester thereof; A′ is a substituted or unsubstituted aryl group; n is an integer of 1 or 2; and m is an integer of 0 - 4).

Among the bisazo compounds represented by formula (XIV), those which are represented by the following general formula (XIVa) are preferred:

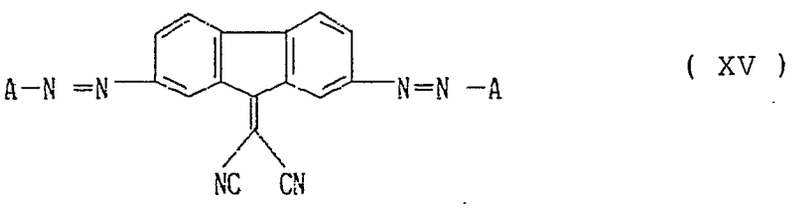


( XIVa)

where $Ar^5$, $Ar^6$ and A have the same meanings as defined for formula (XIV).

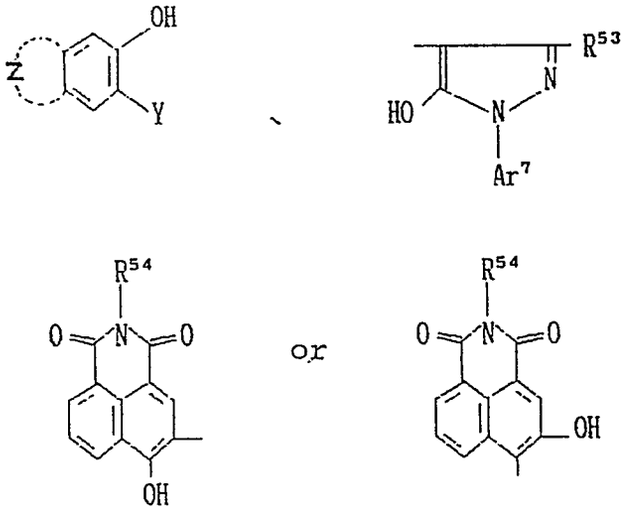
More preferred are those compounds wherein $Ar^5$ and $Ar^6$ in formula (XIVa) each represents a substituted or unsubstituted phenyl group, with the substituent being selected from among an alkyl group such as methyl or ethyl, an alkoxy group such as methoxy or ethoxy, a halogen atom such as chlorine or bromine, a hydroxyl group and a cyano group.

Bisazo compounds represented by the following general formula (XV) are also useful as CGM:



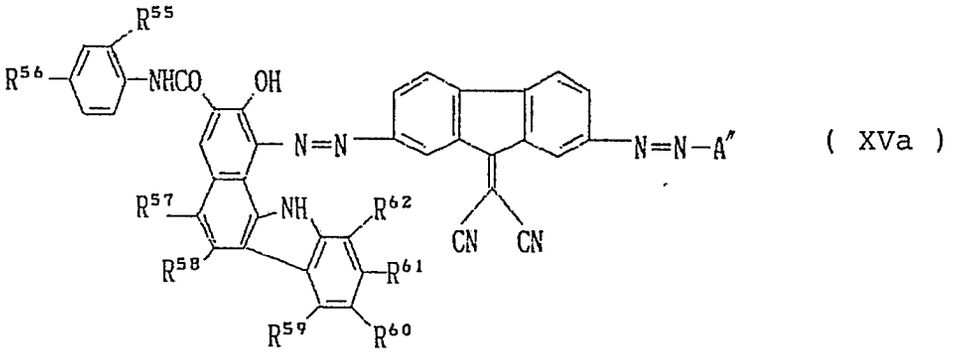
( XV )

where A is



(where Z is the atomic group necessary to form a substituted or unsubstituted aromatic carbon ring or a substituted or unsubstituted aromatic heterocyclic ring; Y is a hydrogen atom, a hydroxyl group, a carboxyl group, an ester group thereof, a sulfo group, a substituted or unsubstituted carbamoyl group, or a substituted or unsubstituted sulfamoyl group; $R^{53}$ is a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted carbamoyl group, a carboxyl group, an ester group thereof, a cyano group; $Ar^7$ is a substituted or unsubstituted aryl group; and $R^{54}$ is a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, or a substituted or unsubstituted aryl group).

Among the bisazo compounds of formula (XV), fluorenylidene group containing bisazo compounds represented by the following general formula (XVa) are particularly effective:

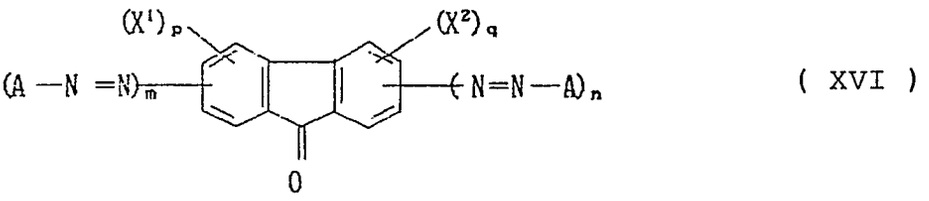


( XVa )

where $R^{55}$ and $R^{56}$ each is an alkyl group, an alkoxy group or an aryl group; $R^{57}$, $R^{58}$, $R^{59}$, $R^{60}$, $R^{61}$ and $R^{62}$ each is a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a hydroxyl group or an aryl group; and A″ is a substituted or unsubstituted aryl group.

The bisazo compounds of formula (XVa) whose intramolecular carbazole group would contribute sensitizing action are capable of providing high sensitivity, particularly in the longer wavelength range. The combination with the intramolecular carbamoyl group moiety provides an effective coupler which exhibits satisfactory sensitivity characteristics over a broad range of wavelengths, thereby contributing to the fabrication of an efficient photoreceptor for use with a semiconductor laser.

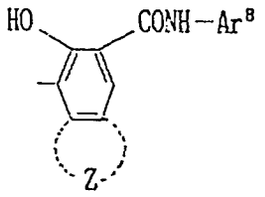
Bisazo compounds represented by the following general formula (XVI) can also be used as carrier generation materials:



( XVI )

where $X^1$ and $X^2$ each is a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a nitro group, a cyano group, a hydroxyl group or a substituted or unsubstituted amino group, provided that at least one of $X^1$ and $X^2$ is a halogen atom; p and q each represents an integer of 0, 1 or 2, provided that p and q are not zero at the same time and that when p is 2, $X^1$ may assume the same or

different groups, and that when q is 2, $X^2$ may assume the same or different groups; and A is a group represented by the following general formula (XVII):



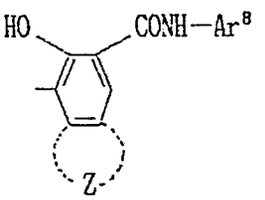
( XVII )

(where $Ar^8$ is an aromatic carbocyclic or heterocyclic group having at least one fluorinated hydrocarbon group; Z is the nonmetallic atomic group necessary to form a substituted or unsubstituted aromatic carbon ring or a substituted or unsubstituted aromatic hetero ring); and m and n each represents an integer of 0, 1 or 2, provided that m and n are not zero at the same time.

Examples of the halogen atom represented by $X^1$ and $X^2$ in formula (XVI) include chlorine, bromine, fluorine and iodine atoms. At least one of $X^1$ and $X^2$ has a halogen atom. The alkyl group represented by $X^1$ and $X^2$ is preferably a substituted or unsubstituted alkyl group having 1 - 4 carbon atoms and illustrative examples include methyl, ethyl, β-cyanoethyl, iso-propyl, trifluoromethyl and t-butyl. The alkoxy group represented by $X^1$ and $X^2$ is preferably a substituted or unsubstituted alkoxy group having 1 - 4 carbon atoms and illustrative examples include methoxy, ethoxy, β-chloroethyl and sec-butoxy. The substituted or unsubstituted amino group represented by $X^1$ and $X^2$ include those which are substituted by an alkyl group, an aryl group (preferably phenyl), etc. such as N-methylamino, N-ethylamino, N,N-dimethylamino, N,N-diethylamino, N-phenylamino and N,N-diphenylamino, and those which are substituted by an acyl group, such as acetylamino and p-chlorobenzoylamino.

In formula (XVI), p and q each represents 0, 1 or 2, provided that p and q are not zero at the same time, and the preferred case is where p = 1 and 1 = 0 or where p = 1 and q = 1. When p or q is 2, $X^1$ and $X^2$ may be the same or different.

In formula (XVI), A is represented by the following general formula (XVII):



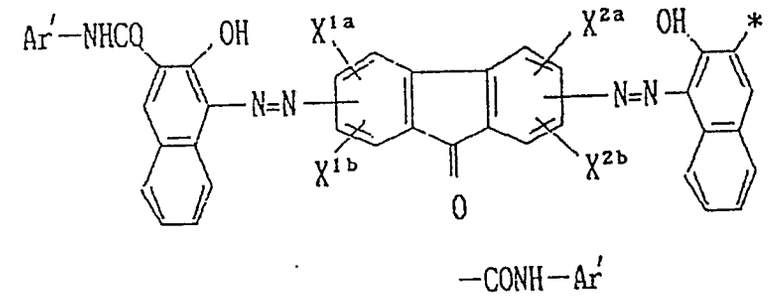
( XVII )

where $Ar^8$ is an aromatic carbocyclic or heterocyclic group having at least one fluorinated hydrocarbon group. The fluorinated hydrocarbon group preferably contains 1 - 4 carbon atoms and may be exemplified by trifluoromethyl, pentafluoroethyl, tetrafluoroethyl, heptafluoropropyl, etc. Trifluoromethyl is more preferred. Illustrative aromatic carbocyclic groups include phenyl, naphthyl and anthryl, with phenyl being preferred. Illustrative aromatic heterocyclic groups include carbazolyl and dibenzofuryl. These aromatic carbocyclic and heterocyclic groups may contain substituents other than the fluorinated hydrocarbon group, and such optional substituents include: a substituted or unsubstituted alkyl group having 1 - 4 carbon atoms such as methyl, ethyl, isopropyl, t-butyl or trifluoromethyl; a substituted or unsubstituted aralkyl group such as benzyl or phenethyl; a halogen atom such as chlorine, bromine, fluorine or iodine; a substituted or unsubstituted alkoxy group having 1 - 4 carbon atoms such as methoxy, ethoxy, isopropoxy, t-butoxy or 2-chloroethoxy; a hydroxyl group; a substituted or unsubstituted aryloxy group such as p-chlorophenoxy or 1-naphtoxy; an acyloxy group such as acetyloxy or p-cyanobenzoyloxy; a carboxyl group or an ester group thereof such as ethoxycarbonyl or m-bromophenoxycarbonyl; a carbamoyl group such as an aminocarbonyl, t-butylaminocarbonyl or anilinocarbonyl; an acyl group such as acetyl or o-nitrobenzoyl; a sulfo group or a sulfamoyl group such as aminosulfonyl, t-butylaminousulfonyl or p-tolylaminosulfonyl; an amino group or an acylamino group such as acetylamino or benzoylamino; a sulfonamido group such as methanesulfonamido or p-toluenesulfonamido; a cyano group; and a nitro group. Among these substituents, the following are preferred: a substituted or unsubstituted alkyl group having 1 - 4 carbon atoms such as methyl, ethyl, isopropyl, t-butyl or trifluoromethyl; a halogen atom such as chlorine, bromine, fluorine or iodine; a substituted or unsubstituted alkoxy group having 1 - 4 carbon atoms such as methoxy, ethoxy, t-butoxy or 2-chloroethoxy; a nitro group; and a cyano group.

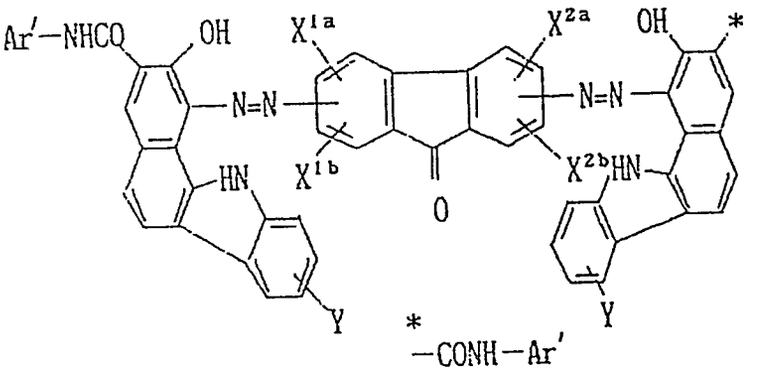
In formula (XVII), Z represents the atomic group necessary to form a substituted or unsubstituted aromatic carbon or heterocyclic ring and may specifically be exemplified by the atomic groups necessary to form a substituted or unsubstituted benzene ring, a substituted or unsubstituted naphthalene ring, a substituted or unsubstituted indole ring, a substituted or unsubstituted carbazole ring, etc. The atomic groups necessary to form these rings may have substituents such as those listed in connection with $Ar^8$ and preferred examples

include a halogen atom ie., chlorine, bromine, fluorine or iodine), a sulfo group and a sulfamoyl group (e.g., aminosulfonyl, p-tolylaminosulfonyl, etc.).

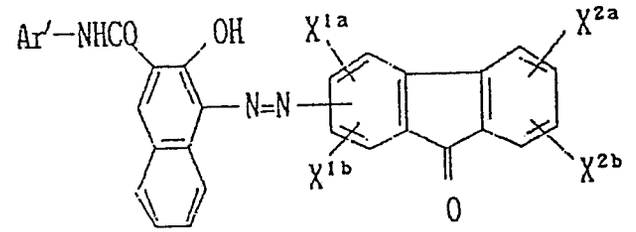
Among the bisazo compounds represented by formula (XVI), those which are represented by the following general formulas (XVIII), (XIV), (XXX) and (XXI) are preferred:



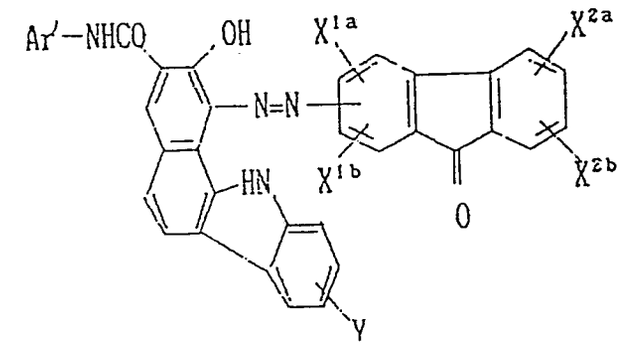
( XVIII )



( XIX )



( XX )



( XXI )

where $X^{1a}$, $X^{1b}$, $X^{2a}$ and $X^{2b}$ each represents a hydrogen atom, a halogen atom, a substituted or unsubstituted

alkyl group, a substituted or unsubstituted alkoxy group, a nitro group, a cyano group, a hydroxyl group or a substituted or unsubstituted amino group, provided that at least one of $X^{1a}$, $X^{1b}$, $X^{2a}$ and $X^{2b}$ is a halogen atom, and that $X^{1a}$ and $X^{1b}$ or $X^{2a}$ and $X^{2b}$ may be the same or different; Ar′ has the same meaning as $Ar^8$ in formula (XVI); Y has the same meaning as the substituent on Z in formula (XVI).

The bisazo compounds represented by the general formula (XVI) can be easily synthesized by known methods.

Synthesis Example (synthesis of compound XVI-71 to be shown hereinafter)

2,7-Diamino-4-bromo-9-fluorenone (2.89 g, 0.01 mol.) is dispersed in 10 ml of HCl and 20 ml of water. Under cooling at 5° C or below, a solution having 1.40 g (0.02 mol) of sodium nitrite dissolved in 5 ml of water is added dropwise to the dispersion. Under continued stirring for 1 h at the same temperature, the insoluble matter is removed by filtration and a solution having 4.6 g of ammonium hexafluorophosphate in 50 ml of water is added to the filtrate. The precipitating tetrazonium salt is recovered by filtration and dissolved in 100 ml of N,N-dimethylformamide (DMF). Under cooling at 5° C or below, a solution having 6.62 g (0.02 mol) of 2-hydroxy-3-naphthoic acid-3′-trifluoromethylanilide dissolved in 200 ml of DMF is added dropwise.

Under continued cooling at 5° C or below, a solution having 6 g (0.04 mol) of triethanolamine dissolved in 30 ml of DMF is added dropwise and the mixture is stirred for 1 h at 5° C or below, then for additional 4 h at room temperature. After the reaction, the resulting crystal is recovered by filtration, washed successively with DMF and water and finally dried to obtain the end product in an amount of 8.71 g. This product has the following data of elemental analysis: C = 60.5%, H = 2.77%, and N = 8.63% (calculated values), and C = 60.1%, H = 2.95% and N = 8.72% (found values).

Other compounds can be synthesized by similar procedures; first, corresponding amino compounds are used to make diazonium compounds, which are then reacted with 2-hydroxy-3-naphthoic acid-substituted anilide or 2-hydroxy-3-(substituted phenylcarbamoyl) benzo[a]-substituted or unsubstituted carbazole.

The electroconductive base for use in the present invention may be a sheet of metal selected from among, for example, aluminum, nickel, copper, zinc, palladium, silver, indium, tin, platinum, gold, stainless steel, brass, etc. The electroconductive base can also be made by providing an electroconductive layer on an insulating substrate which is suitably selected from among paper, plastic sheets and other materials that are flexible and that have sufficient strength to withstand bending, tensile and other stresses. The electroconductive layer may be formed by various methods including laminating a metal sheet and vacuum evaporating a metal.

The carrier generation layer may be composed of a carrier generation material (CGM) alone or in combination with a suitable binder resin. If desired, a carrier transport material having high mobility of carriers with a specified or unspecified polarity may be incorporated. Specific methods of forming the carrier generation layer include: vacuum evaporating CGM on the electroconductive base described above and; applying or dip-coating CGM which is dissolved or dispersed in a suitable solvent either alone or together with a suitable binder resin, and drying the coating. In the latter method, a binder resin or a carrier transport material may be incorporated and in this case, the proportions of carrier generation material, binder resin and carrier transport material are preferably in the range of 1:(0 - 100):(0 - 500), more preferably in the range of 1:(1 - 10):(0 - 50), on a weight basis.

Constituent layers of the carrier transport layer may be formed by the following process: dissolving or dispersing a carrier transport material and a binder resin in a solvent; coating the solution or dispersion onto the carrier generation layer or other constituent layers of the carrier transport layer; and drying the coated layers.

An intermediate layer or a subbing layer can be formed by coating and drying a solution having a binder resin dissolved in a solvent. Illustrative solvents or dispersants that may be used in this method include: n-butylamine, diethylamine, ethylenediamine isopropanolamine, monoethanolamine, triethanolamine, triethylenediamine, N,N-dimethylformamide, acetone, methyl ethyl ketone, cyclohexanone, benzene, toluene, xylene, chloroform, 1,2-dichloroethane dichloromethane, tetrahydrofuran, dioxane, methanol, ethanol, isopropanol, ethyl acetate, butyl acetate and dimethyl sulfoxide.

Besides the polycarbonates having a structural unit represented by the general formula (I) and/or the general formula (II) as the principal recurring unit, the following resins may be used as binders either on their own or as admixtures: polycarbonates other than those described above, polyesters, methacrylic resins, acrylic resins, polyvinyl chloride, polyvinylidene chloride, polystyrene, polyvinyl acetate, melamine resins, polyurethanes, styrene-acrylate copolymers, styrene-butadiene copolymer, vinylidene chloride-acrylonitrile copolymer, vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinyl acetate-maleic anhydride copolymer, silicone resins, silicone-alkyd resins, phenolic resins, styrene-alkyd resins, poly-N-vinylcarbazole, and polyvinyl butyral.

Other useful resins are transparent resins having a volume resistivity of at least $10^8\Omega\cdot$cm, preferably at least $10^{10}\Omega\cdot$cm, more preferably at least $10^{13}\Omega\cdot$cm. Resins that cure by the action of light or heat may also the used as binders and examples of such photo- or heat-curable resins include thermosetting acrylic resins, epoxy resins, urethane resins, urea resins, polyester resins, alkyd resins, melamine resins and photocurable cinnamic ester resins, as well as copolymerized and condensed resins thereof. All other photo- and heat-curable resins commonly employed in electrophotographic materials may be used in the present invention. In order to provide improved working and physical properties (e.g. prevention of cracking and imparting flexibility), the protective layer may incorporate therein less than 50 wt% of a thermoplastic resin as

required. Usable thermoplastic resins include, for example, polypropylene, acrylic resins, methacrylic resins, vinyl chloride resin, vinyl acetate resin, epoxy resins, polycarbonate resins, copolymerized resins thereof, high-molecular weight organic semiconductors such as poly-N-vinylcarbazole, and any other thermoplastic resins that are commonly used in electrophotographic materials.

Binder resins that are to be used in an intermediate layer or a subbing layer may be selected from among metal oxides such as aluminum oxide and indium oxide and high-molecular weight materials such as acrylic resins, methacrylic resins, vinyl chloride resin, vinyl acetate resin, epoxy resins, polyurethane resins, phenolic resins, polyester resins, alkyd resins, polycarbonate resins, silicone resins, melamine resins, vinyl chloride-vinyl acetate copolymer resin, and vinyl chloride-vinyl acetate-maleic anhydride copolymer resin.

Speaking of the photoreceptors shown in Figs. 1 - 4, the constituent layers 3A, 3B and 3C of the carrier transport layer 3 may employ the same or different binder resins. For example, in order to provide improved light sensitivity, the topmost or outermost constituent layer 3B or 3C may use the polycarbonate of the present invention, with a bisphenol A type polycarbonate being used in the bottommost constituent layer 3A that is the closest to the electroconductive base. If desired, the constituent layer 3A (or 3B) which is adjacent the outermost constituent layer 3B (or 3C) and which is closer to the electro conductive base may be designed to employ a binder resin that is hardly soluble with respect to the solvent used to coat said outermost constituent layer. This offers the advantage of preventing not only diffusion of the carrier transport material into the bottommost constituent layer 3A but also swelling of said layer.

The constituent layer 3B or 3C that is more remote from the electroconductive base may be coated in a different way than the bottommost constituent layer 3A is coated. For instance, the constituent layer 3A may be formed by dip coating whereas the constituent layer 3B or 3C is formed by spray coating, and this is effective in preventing dissolution and swelling of the bottommost constituent layer 3A.

The bottommost constituent layer 3A preferably has a thickness of 5 - 50 μm, with the range of 5 - 30 μm being more preferred. The outermost constituent layer 3B or 3C preferably has a thickness of 0.1 - 30 μm, with the range of 0.5 - 10 μm being more preferred.

The carrier generation layer preferably has a thickness of 0.01 - 10 μm, with the range of 0.1 - 5 μm being more preferred.

The light-sensitive layer may have a high-molecular weight semiconductor contained therein. While various high-molecular weight semiconductors may be used, poly-N-vinylcarbazole and its derivatives are preferred because of their high degree of curability. Derivatives of poly-N-vinylcarbazole are such that all or part of the carbazole rings in the recurring units have various substituents such as an alkyl group, a nitro group, an amino group, a hydroxyl group and a halogen atom.

The light-sensitive layer may also have at least one electron - accepting materials contained therein in order attain various purposes such as improving sensitivity, reducing residual potential and minimizing fatigue that results from cyclic use of the photoreceptor. Exemplary electron-accepting materials that may be used in the photoreceptor of the present invention include: succinic anhydride, maleic anhydride, dibromomaleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, 3-nitrophthalkic anhydride, 4-nitrophthalic anhydride, pyromellitic anhydride, mellitic anhydride, tetracyanoethylene, tetracyanoquinodimethane, o-dinitrobenzene, m-dinitrobenzene, 1,3,5-trinitrobenzene, paranitrobenzonitrile, picryl chloride, quinone chlorimide, chloranyl, bromanyl, 2-methylnaphthoquinone, dichlorodicyanoparabenzoquinone, anthraquinone, dinitroanthraquinone, trinitrofluorenone, 9-fluorenylidene-(dicyanomethylenemalonodinitrile), polynitro-9-fluorenylidene-(dicyanomethylenemalonodinitrile), picric acid, o-nitrobenzoic acid, p-nitrobenzoic acid, 3,5-dinitrobenzoic acid, pentafluorobenzoic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid, phthalic acid, mellitic acid and other compounds having a high degree of electron affinity. These electron-accepting substances may be used either on their own or as admixtures. Among these examples, fluorenone compounds, quinone compounds and benzene derivatives having electron-withdrawing substituents such as Cl, CN and $NO_2$ may be used with particular advantage.

Silicone oil and fluorine containing surfactants may also be incorporated as surface modifiers in the photoreceptor of the present invention. Ammonium compounds may also be incorporated as agents to provide improved durability. Ultraviolet (uv) absorbers may also be incorporated and preferred examples include benzoic acid, stilbene compounds and their derivatives, and nitrogenous compounds such as triazole compounds, imidazole compounds, triazine compounds, coumarin compounds, oxadiazole compounds, thiazole compounds and derivatives thereof.

An antioxidant may be incorporated in the carrier transport layer, the carrier generation layer and the light-sensitive layer. This is effective not only in minimizing the adverse effects of ozone that is generated by discharging but also in preventing the increase in residual potential or decrease in charging potential that might occur during cyclic use of the photoreceptor. Illustrative antioxidants include hindered phenol, hindered amines, paraphenylenediamine, arylalkanes, hydroquinone, spirochromans, spiroindanone and its derivatives, organosulfur compounds, and organo-phosphorus compounds. Specific examples of the compounds that may be used as antioxidants are found in USP serial No. 07/180,816.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Preparation of electrophotographic photoreceptors:

Samples of electrophotographic photoreceptor were prepared as described below.

## EXAMPLE 1

A 100-μm thick electroconductive base made of aluminum-evaporated polyethylene terephthalate was coated with an intermediate layer ca. 0.1 μm thick that was made of a vinyl chloride-vinyl acetate-maleic anhydride copolymer. ("ES-lac MF-10" of Sekisui Chemical Co., Ltd.) In the next step, 4 g of a polycyclic quinone pigment having the structural formula XI-3 shown below was pulverized in a ball mill for 24 h. To the resulting particles, a solution having 2 g of a bisphenol A type polycarbonate ("Panlite L-1250" of Teijin Ltd.) dissolved in 130 ml of 1,2-dichloroethane was added. The mixture was stirred for an additional 24 h to form a dispersion, which was coated by doctor blading onto the previously formed intermediate layer and dried to form a carrier generation layer (CGL) in a thickness of Ca. 0.5 μm.

In the next step, 8 g of a styryl compound (carrier transport material) represented by the structural formula VIII-35 shown hereinafter and 10 g of a polycarbonate ("Panlite L-1250") were dissolved in 100 ml of 1,2-dichloroethane. The resulting solution was coated by doctor blading onto the carrier generation layer and dried at 80°C for 1 h to form a constituent layer of carrier transport layer that was the closest to the electroconductive base in thickness of 18 μm. In this constituent layer, the weight ratio of the content of carrier transport material to binder resin was 80 wt%.

In the next step, 6 g of a styryl compound represented by the structural formula VIII-35 and 10 g of a polycarbonate (viscosity average mol. wt. ca. 30,000) composed of recurring units represented by the structural formula II-2 were dissolved in 100 ml of monochlorobenzene. The resulting solution was coated by doctor blading onto the constituent layer of carrier transport layer that was the closest to the electroconductive base to form the outermost constituent layer of carrier transport layer in a thickness of 4 μm. In this outermost constituent layer, the weight ratio of the content of carrier transport material to binder resin was 60 wt%. Since the solubility of the polycarbonate "Panlite L-1250" in monochlorobenzene was smaller than that of the polycarbonate composed of recurring units represented by the structural formula II-2, the constituent layer of carrier transport layer that was the closest to the electroconductive base would not readily dissolve when the outermost constituent layer was being applied.

## EXAMPLE 1A

An electrophotographic photoreceptor was fabricated as in Example 1 except that the amount of the carrier transport material in the constituent layer of carrier transport layer that was the closest to the electroconductive base was changed from 8 g to 20 g (200%).

## EXAMPLE 2

An intermediate layer and a carrier generation layer were formed as in Example 1. The constituent layer of carrier transport layer that was the closest to the electroconductive base was formed as in Example 1 except that the layer thickness was changed to 19 μm.

In the next step, the outermost constituent layer of carrier transport layer was formed as in Example 1 except that the amount of carrier transport material and the layer thickness were changed to 4 g and 3 μm, respectively.

## COMPARATIVE EXAMPLE 1

An intermediate layer and a carrier generation layer were formed as in Example 1.

In the next step, 8 g of a carrier transport material represented by the structural formula VIII-35 and 10 g of a polycarbonate "Panlite L-1250" were dissolved in 100 ml of 1,2-dichloroethane and the resulting solution was coated onto the carrier generation layer to form a single-layered carrier transport layer in a thickness of 22 μm.

## COMPARATIVE EXAMPLE 1A

Another comparative photoreceptor was prepared by the following procedures. In the first step, an intermediate layer and a carrier generation layer were formed as in Example 1. In the next step, the constituent layers of the carrier transport layer that was the closest to the electroconductive base and the outermost constituent layer of the carrier transport layer were successively formed as in Example 1, except that the content of the carrier transport material in the constituent layer of the carrier transport layer that was the closest to the electroconductive base and its thickness were changed to 4 g and 19 μm, respectively, and that

the content of the carrier transport material in the outermost constituent layer and its thickness were changed to 8 g and 3 μm, respectively.

## COMPARATIVE EXAMPLE 1B

Still another comparative photoreceptor was prepared as in Example 1 except that a bisphenol A type polycarbonate "Panlite L-1250" was used as a binder resin in the outermost constituent layer of carrier transport layer.

## EXAMPLE 3

An intermediate layer and a carrier generation layer were formed as in Example 1 except that a fluorenone compound represented by the structural formula XVI-71 shown hereinafter was used as a carrier generation material.

In the next place, 10 g of a polycarbonate composed of recurring units represented by the general structural formula II-2 and 10 g of a carrier transport material represented by the structural formula VIII-38 also shown hereinafter were dissolved in 100 ml of monochlorobenzene. The resulting solution was coated onto the carrier generation layer to form a constituent layer of the carrier transport layer that was the closest to the electroconductive base in a thickness of 15 μm.

A coating solution for the outermost constituent layer was prepared as described above except that the content of the carrier transport material was reduced to 7 g. This solution was spray-coated onto the constituent layer of the carrier transport layer that was the closest to the electroconductive base to form the outermost constituent layer in a thickness of 5 μm.

## EXAMPLE 4

An electrophotographic photoreceptor was prepared as in Example 3, except that the thickness of the constituent layer of the carrier transport layer that was the closest to the electroconductive base, the content of the carrier transport material in the outermost constituent layer and its thickness were changed to 17 μm, 5 g and 3 μm, respectively.

## EXAMPLE 5

An electrophotographic photoreceptor was prepared as in Example 3, except that the thickness of the constituent layer of the carrier transport layer that was the closest to the electroconductive base, the content of the carrier transport material in the outermost constituent layer and its thickness were changed to 18 μm, 3 g and 2 μm, respectively.

## COMPARATIVE EXAMPLE 3

An intermediate layer and a carrier generation layer were formed as in Example 3.

In the next step, a coating solution of the same composition as that of the solution for forming the constituent layer of carrier transport layer that was the closest to the electroconductive base in Example 3 (containing 10 g of the carrier transport material) was coated onto the carrier generation layer by doctor blading to form a single-layered carrier transport layer in a thickness of 20 μm.

## COMPARATIVE EXAMPLE 4

An additional comparative electrophotographic photoreceptor was prepared as in Comparative Example 3 except that the content of the carrier transport material in the carrier transport layer was changed to 3 g.

## EXAMPLE 6

An intermediate layer was formed as in Example 1.

In the next step, a carrier generation layer was formed as in Example 1 except that a bisazo compound represented by the structural formula XIV-5 shown hereinafter was used as a carrier generation material and that a polyester resin "Vylon-200" of Toyobo Co., Ltd. was used as a binder resin.

Subsequently, 10 g of a carrier transport material having the structural formula X-2 shown hereinafter and 10

g of poly-N-vinylcarbazole "Ruvican M-170" of BASE A.G. were dissolved in 100 ml of tetrahydrofuran (THF) and the resulting solution was coated onto the carrier generation layer by doctor blading to form the constituent layer of carrier transport layer that was the closest to the electroconductive base in a thickness of 18 μm.

In the next place, 6 g of a carrier transport material represented by the structural formula X-2 and 10 g of a polycarbonate composed of structural units represented by the formula II-2 were dissolved in 100 ml of 1,2-dichloroethane, and the resulting solution was coated onto the constituent layer that was closest to the electroconductive base by doctor blading to form the outermost constituent layer in a thickness of 4 μm.

## EXAMPLE 7

An electrophotographic photoreceptor was prepared as in Example 6, except that the thickness of the constituent layer of carrier transport layer that was the closest to the electroconductive base, the thickness of the outermost constituent layer and the weight ratio of the content of carrier transport material to binder resin in the outermost constituent layer were changed to 19 μm, 3 μm and 40%, respectively.

## COMPARATIVE EXAMPLE 6

An intermediate layer and a carrier generation layer were formed as in Example 6. In the next step, a coating solution of the same composition as that of the solution for forming the constituent layer of carrier transport layer that was the closest to the electroconductive base in Example 6 was prepared and coated onto the carrier generation layer by doctor blading to form a single-layered carrier transport layer in a thickness of 22 μm.

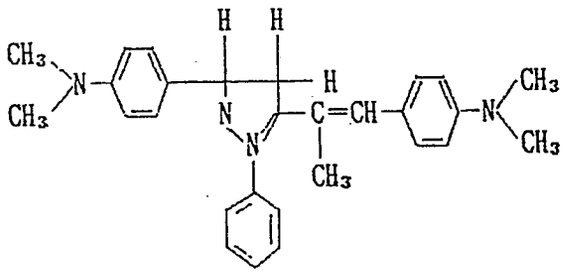
## EXAMPLE 8

An intermediate layer and a carrier generation layer were formed as in Example 1.

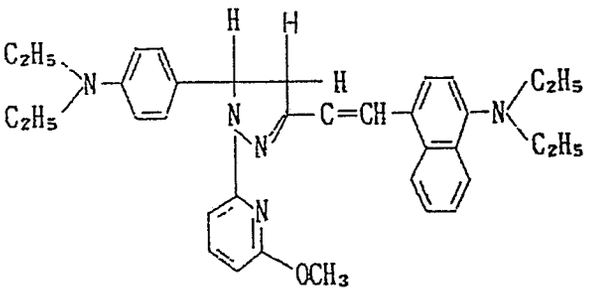
In the next step, 8 g of a pyrazoline compound represented by the structural formula VII-22 shown below and 10 g of a polycarbonate "Panlite L-1250" were dissolved in 100 ml of 1,2-dichloroethane and the resulting solution was coated onto the carrier generation layer to form the constituent layer of carrier transport layer that was the closest to the electroconductive base in a thickness of 18 μm.

Subsequently, 6 g of a pyrazoline compound represented by the structural formula VII-22 and 10 g of a polycarbonate composed of structural units represented by the formula II-5 were dissolved in 100 ml of monochlorobenzene, and the resulting solution was coated onto the constituent layer of carrier transport layer that was the closest to the electroconductive base by doctor blading to form the outermost constituent layer in a thickness of 4 μm.

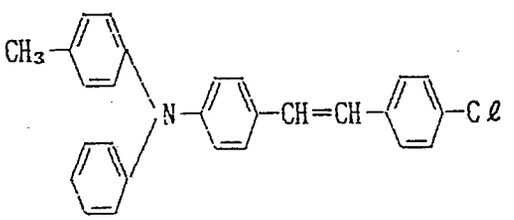
Structural formulas



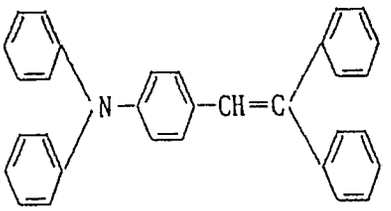
( V-2 )



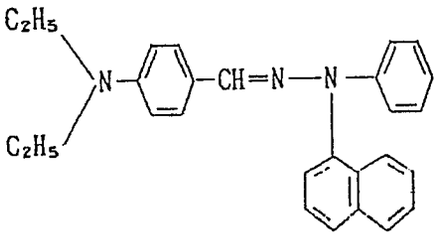
( VII-22 )



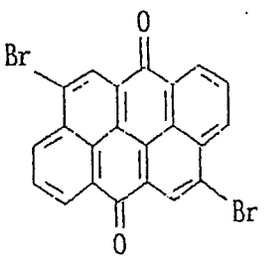
( VIII-35 )



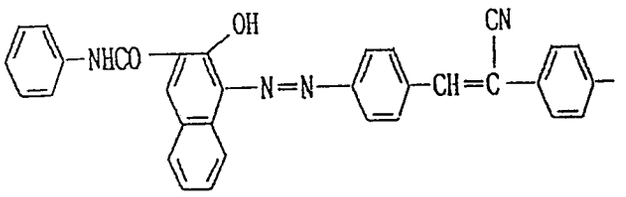
( VIII-38 )



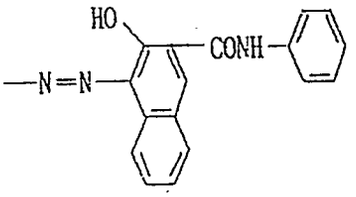
( X-2 )

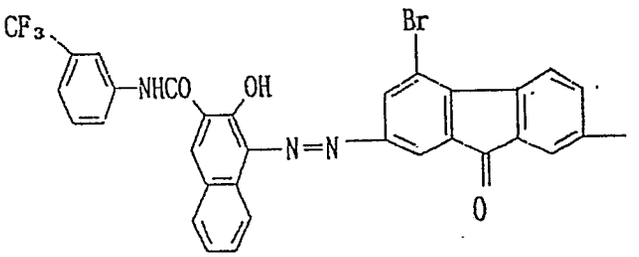


( XI-3 )

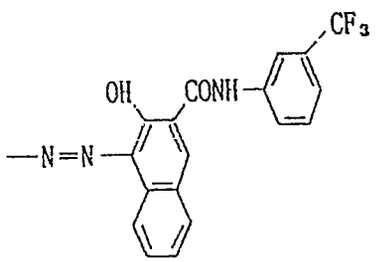


( XIV-5 )





( XVI-71 )



Evaluating the characteristics of photoreceptors:

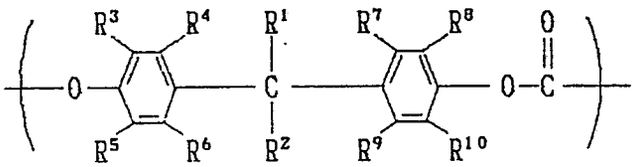
The samples of electrophotographic photoreceptors prepared in Examples 1 - 8 and Comparative Examples 1 - 6 were set on a copying machine adapted from U-Bix 1550 MR of Konica Corp. and a copying test was conducted through $5 \times 10^4$ cycles. At the same time, measurements were conducted for black paper potential $V_B$ and white paper potential $V_W$. After taking $5 \times 10^4$ copies, checking was made for the amount of decrease in photoreceptor's thickness by wear and for the occurrence of scratches on image surface. The values of $V_B$ and $V_W$ measured before copying and after copying $5 \times 10^4$ sheets, as well as the variations in the respective values ($\Delta|V_B|$ and $\Delta|V_W|$) are shown in Fig. 5.

The term "black paper potential" means the surface potential which developed on a photoreceptor when it was subjected to the cyclic copying test described above using a black paper original having a reflection density of 1.3. The term "white paper potential" means the surface potential which developed on the same photoreceptor when used with a white paper original.

As the data in Fig. 5 shows, the photoreceptor samples prepared in Examples 1 - 8 were high in wear and scratch resistance, showed satisfactory values of both black paper and white paper potential, and permitted a great number of copies to be taken to produce image of consistent quality with minimum variations in the values of black paper and white paper potential.

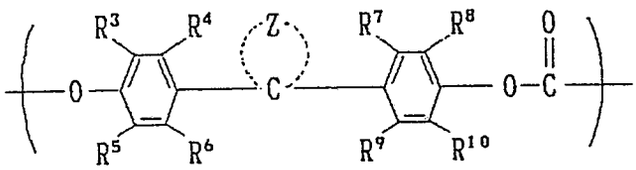
## Claims

1. In a photoreceptor comprising an electroconductive base that has a carrier generation layer formed thereon which is overlaid with a carrier transport layer, the improvement wherein said carrier transport layer comprises at least two constituent layers, the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is closer to said electroconductive base is higher than the weight ratio of the content of the carrier transport material to the binder material in a constituent layer which is more remote from said electroconductive base, and the binder in the outermost constituent layer of said carrier transport layer contains a polycarbonate having as the principal recurring unit a structural unit represented by the following general formula (I) and/or a structural unit represented by the following general formula (II):



( I )

(where $R^1$ and $R^2$ each is a hydrogen atom, a substituted or unsubstituted aliphatic group, a substituted or unsubstituted carbocyclic group, or a substituted or unsubstituted aromatic group, provided that at least one of $R^1$ and $R^2$ is a "bulky" group; and $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is a hydrogen atom, a halogen atom, a substituted or unsubstituted aliphatic group, or a substituted or unsubstituted carbocyclic group);



( II )

(where $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$ and $R^{10}$ each is name as defined above; Z is the atomic group necessary to form a substituted or unsubstituted carbon ring or a substituted or unsubstituted heterocyclic ring).

2. A photoreceptor according to claim 1 wherein the ratio of the content of the carrier transport material to binder material in the outermost constituent layer of said carrier transport layer is not higher than 70 wt%.

3. A photoreceptor according to claim 1 wherein the weight ratio of the content of the carrier transport material to binder material in the outermost constituent layer of said carrier transport layer is 5 - 70 wt%.

4. A photoreceptor according to claim 1 wherein the weight ratio of the content of the carrier transport material to binder material in a constituent layer of said carrier transport layer which is the closest to the electroconductive base is at least 30 wt%.

5. A photoreceptor according to claim 1 wherein the ratio of the content of the carrier transport material to binder material in a constituent layer of said carrier transport layer which is the closest to the electroconductive base is 30 - 300 wt%.

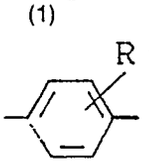
6. A photoreceptor according to claim 1 wherein the ratio of the content of the carrier transport material to binder material in the outermost constituent layer of said carrier transport layer differs by at least 1.0 wt% from the ratio of the content of the carrier transport material to binder material in a constituent layer which is the closest to the electroconductive base.

7. A photoreceptor according to claim 1 wherein $R^1$ and $R^2$ in said general formula (I) represent different groups, or they are bound asymmetrically if they are of the same group.

8. A photoreceptor according to claim 1 wherein at least one of $R^1$ and $R^2$ in said general formula (I) is a bulky group having at least 3 carbon atoms.

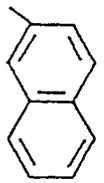
9. A photoreceptor according to claim 8 wherein at least one of said $R^1$ and $R^2$ is a member selected from among the following groups:

(1)



where $R^{11}$ is a hydrogen atom, an alkyl group such as methyl, or an alkyl ester group represented by $+CH_2)_m COOR$ (where R is an alkyl group, and $m \geqq 1$);

(2)



(3) an alkyl group represented by $-C_mH_{2m+1}$ ($m \geqq 4$); and

(4) an alkyl ester group represented by $+CH_2)_m COOR^{12}$ (where $R^{12}$ is an alkyl group, and $m \geqq 2$).

10. A photoreceptor according to claim 1 wherein each of $R^3$ - $R^{10}$ in said general formulas (I) and (II) is at least one member selected from the group consisting of a hydrogen atom, a halogen atom, a methyl group and a cyclohexyl group.

11. A photoreceptor according to claim 1 wherein Z in the general formula (II) forms a 5- or 6-membered carbon ring or heterocyclic ring.

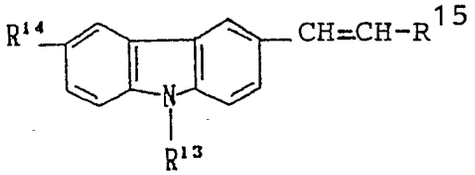
12. A photoreceptor according to claim 1 wherein the number of repetitions of the structural unit represented by said general formula (I) or (II) is from 10 to 5000.

13. A photoreceptor according to claim 1 wherein the number of repetitions of the structural unit represented by said general formula (I) or (II) is from 5o to 2000.

14. A photoreceptor according to claim 1 wherein said polycarbonate has at least a structural unit represented by said general formula (II).

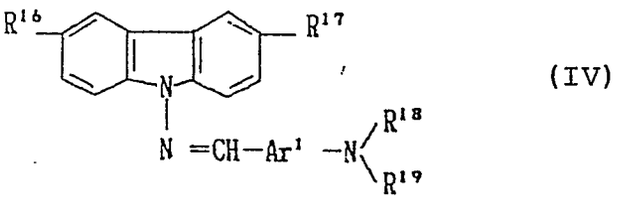
15. A photoreceptor according to claim 11 wherein $R^3$ - $R^{10}$ in said general formula (II) are each a hydrogen atom and Z is the atomic group necessary to form a cyclohexylidene group.

16. A photoreceptor according to claim 1 wherein said carrier transport material is at least one of the members represented by the following general formulas (III) - (X):



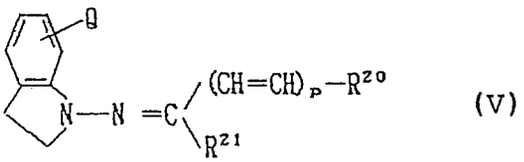
( III )

(where $R^{13}$ is a substituted or unsubstituted aryl group; $R^{14}$ is a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, an alkoxy group, an amino group, a hydroxyl group or a substituted amino group; and $R^{15}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group);



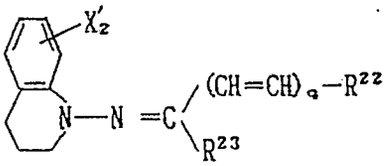
(IV)

(where $R^{16}$ and $R^{17}$ each is a hydrogen atom or a halogen atom; $R^{18}$ and $R^{19}$ each is a substituted or unsubstituted aryl group; and $Ar^1$ is a substituted or unsubstituted arylene group);



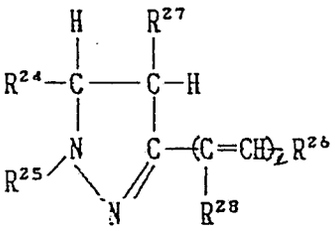
(V)

(where $R^{20}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; $R^{21}$ is a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; Q is a hydrogen atom, a halogen atom, an alkyl group, a substituted amino group, an alkoxy group or a cyano group; and p is an integer of 0 or 1);



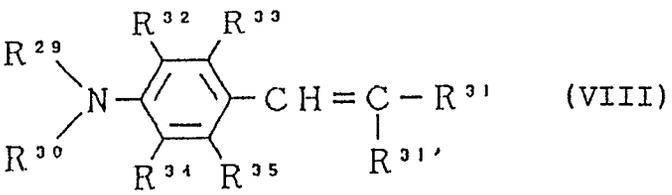
(VI)

(where $R^{22}$ is a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group; $R^{23}$ is a hydrogen atom, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group; $X'_2$ is a hydrogen atom, a halogen atom, an alkyl group, a substituted amino group, an alkoxy group or a cyano group; and q is an integer of 0 or 1);



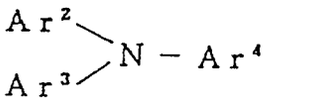
(VII)

(where $\ell$ is an integer of 0 or 1; $R^{24}$, $R^{25}$ and $R^{26}$ each is a substituted or unsubstituted aryl group; $R^{27}$ and $R^{28}$ each is a hydrogen atom, an alkyl group having 1 - 4 carbon atoms, a substituted or unsubstituted aryl or aralkyl group, provided that $R^{27}$ and $R^{28}$ are not a hydrogen atom at the same time, and when $\ell$ is 0, $R^{27}$ is not a hydrogen atom);



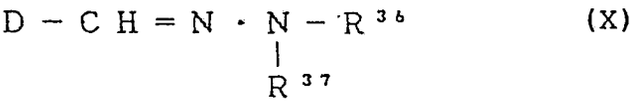
(VIII)

(where $R^{29}$ and $R^{30}$ each is a substituted or unsubstituted alkyl or phenyl group, with the substituent being an alkyl, alkoxy or phenyl group; $R^{31}$ is a substituted or unsubstituted phenyl, naphthyl, anthryl, fluorenyl or heterocyclic group, with the substituent being an alkyl group, an alkoxy group, a halogen atom, a hydroxyl group or a phenyl group; $R^{31'}$ is a hydrogen atom, a substituted or unsubstituted alkyl or phenyl group; and $R^{32}$, $R^{33}$, $R^{34}$ and $R^{35}$ each is a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group or an alkylamino group);



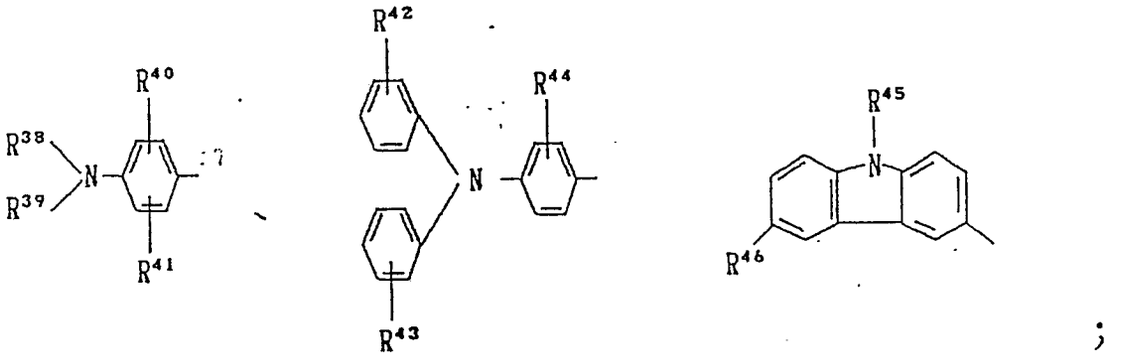
(IX)

(where $Ar^2$ and $Ar^3$ each is a substituted or unsubstituted phenyl group, with the substituent being a halogen atom, an alkyl group, a nitro group or an alkoxy group; and $Ar^4$ is a substituted or unsubstituted phenyl, naphthyl, anthryl, fluorenyl or heterocyclic group, with the substituent being an alkyl group, an alkoxy group, a halogen atom, a hydroxyl group, an aryloxy group, an aryl group, an amino group, a nitro group, a piperidino group, a morpholino group, a naphthyl group, an anthryl group or a substituted amino group, provided that the last-mentioned substituted amino group has an acyl, alkyl, aryl or aralkyl group as the substituent);



(X)

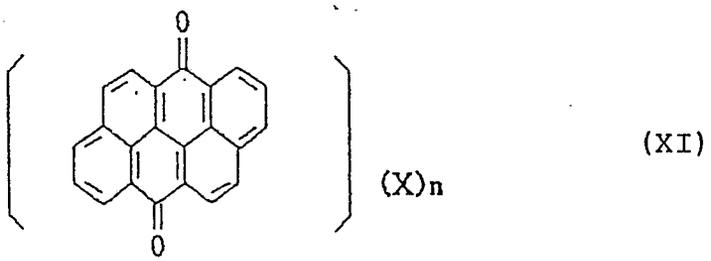
(where D is a substituted or unsubstituted phenyl group or a substituted or unsubstituted carbazolyl group, as specifically illustrated by



where $R^{36}$, $R^{37}$, $R^{38}$, $R^{39}$ and $R^{45}$ each represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group or a substituted or unsubstituted aryl group; and $R^{40}$, $R^{41}$, $R^{42}$, $R^{43}$, $R^{44}$ and $R^{46}$ each represents an alkyl group, an alkoxy group, a halogen atom, etc.)

17. A photoreceptor according to claim 1 wherein the carrier generation material contained in said carrier generation layer is a polycyclic quinone pigment or a bisazo pigment.

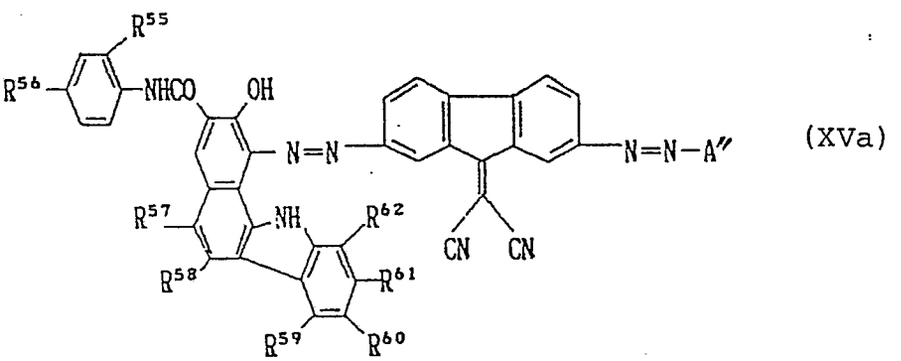
18. A photoreceptor according to claim 17 wherein said polycyclic quinone pigment is anthanthrone pigment represented by the following general formula (XI):



(XI)

where X is a halogen atom, a nitro group, a cyano group, an acyl group or a carboxyl group; n is an integer of 0 to 4; and m is an integer of 0 to 6.

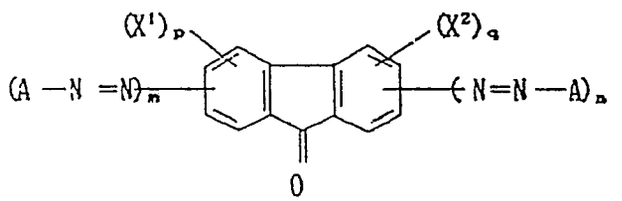
19. A photoreceptor according to claim 17 wherein said bisazo pigment is fluorenylidene pigment represented by the following general formula (XVa):



(XVa)

where $R^{55}$ and $R^{56}$ each is an alkyl group, an alkoxy group or an aryl group; $R^{57}$, $R^{58}$, $R^{59}$, $R^{60}$, $R^{61}$ and $R^{62}$ each is a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, an amino group, a hydroxyl group or an aryl group; and A″ is a substituted or unsubstituted aryl group.

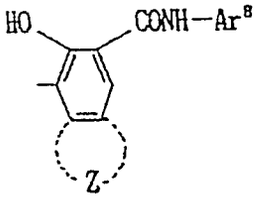
20. A photoreceptor according to claim 17 wherein said bisazo pigment is a fluorenone pigment represented by the following general formula (XVI):



(XVI)

where $X^1$ and $X^2$ each is a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, a nitro group, a cyano group, a hydroxyl group or a substituted or

unsubstituted amino group, provided that at least one of $X^1$ and $X^2$ is a halogen atom; p and q each represents an integer of 0, 1 or 2, provided that p and q are not zero at the same time and that when p is 2, $X^1$ may be the same or different groups, and that when q is 2, $X^2$ may be the same or different groups; and A is a group represented by the following general formula (XVII):



(XVII)

(where $Ar^8$ is an aromatic carbocyclic or heterocyclic group having at least one fluorinated hydrocarbon group; Z is the nonmetallic atomic group necessary to form a substituted or unsubstituted aromatic carbon ring or a substituted or unsubstituted aromatic heterocyclic ring); m and n each represents an integer of 0, 1 or 2, provided that m and n are not zero at the same time.

21. A photoreceptor according to claim 1 wherein a constituent layer of said carrier transport layer that is closer to the electroconductive base and that is adjacent to the outermost constituent layer of said carrier transport layer contains a bisphenol A type polycarbonate as a binder.

22. A photoreceptor according to claim 1 wherein the binder resin contained in a constituent layer of said carrier transport layer that is closer to the electroconductive base and that is adjacent to the outermost constituent layer of said carrier transport layer is hardly soluble with respect to the solvent used to coat said outermost constituent layer.

23. A photoreceptor according to claim 1 wherein a constituent layer of said carrier transport layer that is the closest to the electroconductive base is formed by dip coating, and a constituent layer of said carrier transport layer that is adjacent to said constituent layer and that is more remote from the electroconductive base is formed by spray coating.

24. A photoreceptor according to claim 1 wherein a constituent layer of said carrier transport layer which is the closest to the conductive base has a thickness of 5 -50 μm.

25. A photoreceptor according to claim 1 wherein a constituent layer of said carrier transport layer which is the closest to the electroconductive base has a thickness of 5 - 30 μm.

26. A photoreceptor according to claim 1 wherein the outermost constituent layer of said carrier transport layer has a thickness of 0.1 - 30 μm.

27. A photoreceptor according to claim 1 wherein the outermost constituent layer of said carrier transport layer has a thickness of 0.5 - 10 μm.

28. A photoreceptor according to claim 1 wherein said carrier generation layer has a thickness of 0.01 - 10 μm.

29. A photoreceptor according to claim 1 wherein said carrier generation layer has a thickness of 0.1 - 5 μm.

FIG.1

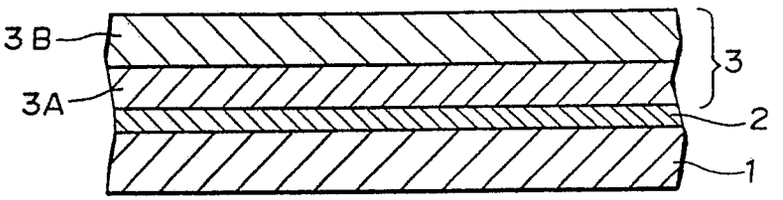



FIG.2

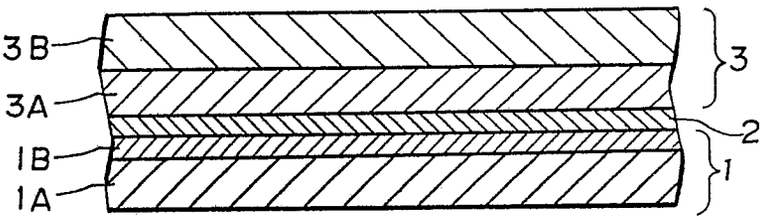



FIG.3

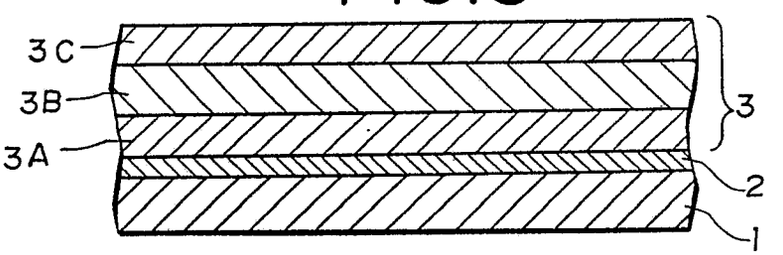
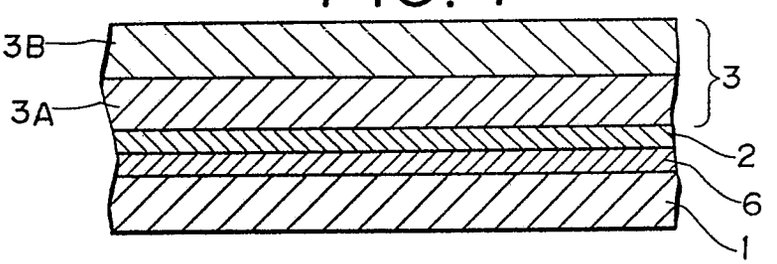



FIG.4



| | Constituent layer (Ⅰ) of CTL | | | Constituent layer (Ⅱ) of CTL | | | Initial | | After copying through $5\times10^4$ cycles | | Variations | | Scrach on image | Wear ($\mu$m) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | binder resin | CTM content (%) | thickness ($\mu$m) | binder resin | CTM content (%) | thickness ($\mu$m) | $V_B$ (V) | $V_W$ (V) | $V_B$ (V) | $V_W$ (V) | $\Delta\lvert V_B\rvert$ (V) | $\Delta\lvert V_W\rvert$ (V) | | |
| Example 1 | BPA | 80 | 18 | Ⅱ-2 | 60 | 4 | −655 | −55 | −670 | −85 | 20 | 30 | none | 0.6 |
| Example 1A | BPA | 200 | 18 | Ⅱ-2 | 60 | 4 | −650 | −40 | −660 | −50 | 10 | 10 | none | 0.6 |
| Example 2 | BPA | 80 | 19 | Ⅱ-2 | 40 | 3 | −655 | −60 | −675 | −90 | 20 | 30 | none | 0.4 |
| Comparative Example 1 | | | | BPA | 80 | 22 | −650 | −60 | −690 | −120 | 40 | 60 | occurred after $3\times10^4$ cycles | 2.9 |
| Comparative Example 1A | BPA | 40 | 19 | Ⅱ-2 | 80 | 3 | −710 | −130 | −730 | −170 | 20 | 40 | occurred after $4\times10^4$ cycles | 1.6 |
| Comparative Example 1B | BPA | 80 | 18 | BPA | 60 | 4 | −690 | −70 | −710 | −100 | 20 | 30 | occurred after $4\times10^4$ cycles | 1.4 |
| Example 3 | Ⅱ-2 | 100 | 15 | Ⅱ-2* | 70 | 5 | −660 | −60 | −680 | −90 | 20 | 30 | none | 0.8 |
| Example 4 | Ⅱ-2 | 100 | 17 | Ⅱ-2* | 50 | 3 | −665 | −60 | −680 | −85 | 15 | 15 | none | 0.5 |
| Example 5 | Ⅱ-2 | 100 | 18 | Ⅱ-2* | 30 | 2 | −670 | −65 | −685 | −90 | 15 | 25 | none | 0.3 |
| Comparative Example 3 | | | | Ⅱ-2 | 100 | 20 | −650 | −65 | −700 | −100 | 50 | 35 | occurred after $3\times10^4$ cycles | 2.0 |
| Comparative Example 4 | | | | Ⅱ-2 | 30 | 20 | −680 | −160 | −700 | −200 | 20 | 40 | none | 0.3 |
| Example 6 | PVK | 100 | 18 | Ⅱ-2 | 60 | 4 | −670 | −90 | −705 | −110 | 35 | 20 | none | 0.6 |
| Example 7 | PVK | 100 | 19 | Ⅱ-2 | 40 | 3 | −675 | −85 | −715 | −105 | 40 | 20 | none | 0.4 |
| Comparative Example 6 | | | | PVK | 100 | 22 | −660 | −90 | −720 | −120 | 60 | 30 | occurred after $10^4$ cycles | 5.3 |
| Example 8 | BPA | 80 | 18 | Ⅱ-5 | 60 | 4 | −700 | −60 | −720 | −80 | 20 | 20 | none | 0.7 |

CTL: carrier transport layer

CTM: carrier transport material

BPA: polycarbonate "Panlite L-1250"

PVK: polyvinyl carbazole

*: spray coated

Constituent layer (Ⅰ) of CTL: Constituent layer of CTL that is the closest to the electroconductive base

Constituent layer (Ⅱ) of CTL: Outermost constituent layer of CTL or singlelayered CTL

Fig. 5

EP 0 356 246 A2