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(54) Method of image formation

Bilderzeugungsverfahren

Méthode de formation d'image

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(56) References cited:
EP-A- 0 356 246
DE-A- 3 804 449
GB-A- 2 211 954
US-A- 4 800 412

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 481 747 B1

Description

FIELD OF THE INVENTION

The present invention relates to a method of image formation wherein an organic photoelectroconductive photoreceptor is used to form an image at high speed.

BACKGROUND OF THE INVENTION

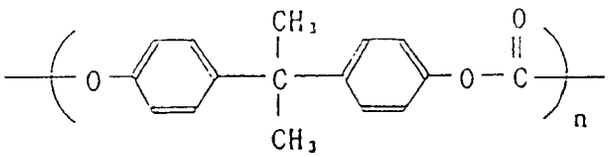
Traditionally, the Carlson method has been commonly used for electrophotographic image formation. In the Carlson method, uniformly charging the surface of photoreceptor is followed by imagewise exposure to form an electrostatic latent image, which is subjected to toner development to form a toner image, which is transferred and fixed onto a transferee to form a final image. The photoreceptor after being used for transfer is subjected to surface discharging using a discharger and residual toner removal using a cleaning blade, cleaning brush or another cleaning device, whereby it is prepared for subsequent long-term repeated use.

Therefore, the electrophotographic photoreceptor is required to have good physical properties such as printability, wear resistance and moisture resistance in repeated use and to have resistance (environmental endurance) to ozone generated upon corona discharge and to ultraviolet rays generated upon exposure, as well as having good charging properties and electrophotographic properties such as high sensitivity and low dark decay.

Traditionally, inorganic photoreceptors have been widely used as electrophotographic photoreceptors whose light-sensitive layer is based on an inorganic photoelectroconductive substance such as selenium, zinc oxide or cadmium sulfide.

In recent years, there has been a trend toward development of organic electrophotographic photoreceptors with high sensitivity and high durability in which the carrier generation and carrier transport functions are allotted to different substances in a light-sensitive layer. These substances are selected from a wide range to exhibit the respective functions according to the desired characteristics.

As a binder for such photoreceptors, a polycarbonate of the bisphenol A type represented by the following formula is well known to have good properties in terms of charging, sensitivity, residual potential and suitability for repeated use,



However, investigations by the inventors have revealed that the polycarbonate of the bisphenol A type is faulty in that its solution becomes unusable in some 1 to 2 weeks because it is liable to gel due to the high crystallinity of the polymer. Also, when a film is formed by coating, crystalline polycarbonate is likely to separate and cause bumps on the film surface during coating, which can cause film tailing and reduce the yield, or which allows the uncleaned toner to remain on the photoreceptor after use and results in imaging failure due to poor cleaning.

In addition, the electrophotographic photoreceptor incorporating the polycarbonate of the bisphenol A as a binder resin, when repeatedly used for image formation over a long period has problems of damaging of the light-sensitive layer surface due to abrasion by a magnetic brush or a cleaning blade and of gradual wear of the light-sensitive layer.

As stated above, the polycarbonate of the bisphenol A type poses problems in storage stability of solutions during preparation of photoreceptors and in the resistance of the photoreceptor surface to mechanical abrasion. With the aim of solving these problems, a number of polycarbonates with different structures have been proposed.

For example, polycarbonates have been proposed in which a fluorine atom is substituted for a hydrogen atom of the alkyl group bound to the central carbon atom between the phenylene rings [Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 65444/1989], a polycarbonate in which an alkyl group or halogen atom substituent is included at the meta-position of the phenylene ring (Japanese Patent O.P.I. Publication No. 148263/1988), a polycarbonate in which a phenyl group or cyclohexyl group substituent is included at the meta-position of the phenylene ring (Japanese Patent O.P.I. Publication No. 269942/1989 or 269943/1989) and a polycarbonate in which a cyclohexyl ring including the central carbon atom is formed between the phenylene rings (U.S. Patent No. 4,931,372). Having a bulky substituent in their structure, the polycarbonates described in these patent publications surpass the polycarbonate of the bisphenol A type in solution stability during preparation of a photoreceptor, in stability against ozone during image formation and in mechanical wear resistance.

It should be noted, however, that the recent increase in demands for photocopies has spurred R & D activities for photocopying machines and relevant articles; for example, high speed copying machines capable of generating 50 or more copies per minute with high resolutions of 6 or more lines/mm have been demanded. In forming an image while rotating the photoreceptor at high speed, the photoreceptor more frequently undergoes photoelectric shocks from an exposure device, a charger, a transfer device and other devices and mechanical shocks from the magnetic brush of a developing device, the blade of a cleaning apparatus and other devices. Particularly, the developing agent on the sleeve of a developing device is liable to be scattered by centrifugal force, since the sleeve is usually rotated at a peripheral speed higher than that of the photoreceptor. To prevent this, it is necessary to increase the magnetic field intensity to constrain the developing agent on the sleeve. When the magnetic field intensity on the sleeve is increased, a hard magnetic brush forms on the sleeve, which strongly abrades the photoreceptor surface and deteriorates the photoreceptor.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of image formation which makes it possible to form an image with high density and high resolution without associated fatigue deterioration or toner scattering by the use of an improved photoreceptor useful even for repeated image formation at high speed.

The inventors made by way of trial a very large number of organic photoreceptors using one or more of the polycarbonates described in the above-mentioned and other publications as binder resins, and subjected them to repeated runs of testing for a long time with the sample loaded on a high speed testing machine rotating at a peripheral speed of not less than 300 mm/sec. The inventors thus discovered a photoreceptor suitable for use in high speed copying machines and developed a method of image formation which makes it possible to obtain high quality images at high speed without being accompanied by developing agent scattering.

BRIEF DESCRIPTION OF THE DRAWINGS

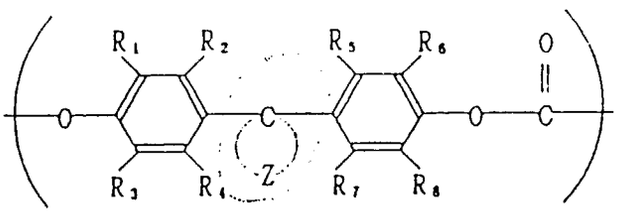
Figures 1 to 6 are cross-sectional views showing the structural configuration of the photoreceptor used in the present invention. Figure 7 is a schematic diagram of an image forming apparatus illustrating the method of image formation of the present invention.

In these figures, the reference numerals denote a support 1, a carrier generation layer 2, a carrier transport layer 3, a light-sensitive layer 4, an original 10, reflective mirrors 14a, 14b, 14c and 14d, a charger 16, a developing apparatus 17, a main developing magnetic pole 17d, a photoreceptor 20 and a cleaning apparatus 21, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The object described above can be accomplished by a method of image formation including a process in which an organic photoelectroconductive photoreceptor being rotated at high speed is subjected to charging and imagewise exposure to form an electrostatic latent image and transporting a developing agent from a sleeve rotating around the periphery of an immobilized magnet having a main developing magnetic pole to develop the electrostatic latent image, wherein said photoreceptor comprises a polycarbonate based on the repeat unit represented by Formulae I or II below contained in at least the uppermost layer constituting the light-sensitive layer configuration, said photoreceptor being rotated at a peripheral speed of at least 300 mm/sec and the magnetic flux density of the main developing magnetic pole on the sleeve exceeding 950 gauss.

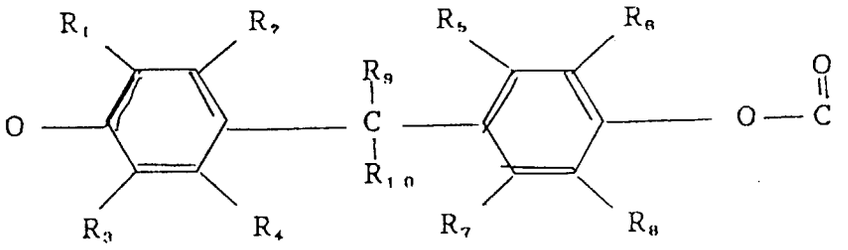
Formula I



wherein Z represents a group of atoms necessary to complete a substituted or unsubstituted carbon ring or heterocyclic

ring group. R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, methyl group, chlorine atom or bromine atom, and not all the substituents are hydrogen atoms at the same time.

Formula II



wherein R_1 to R_8 are as defined in Formula I, and R_9 and R_{10} represents a hydrogen atom or alkyl group having 1 to 6 carbon atoms.

In the method of image formation of the present invention, photocopies are generated at a high speed, for example, 50 copies or more per minute for A4-size landscape position while rotating an organic photoelectroconductive photoreceptor in a drum or belt form (hereinafter simply referred to as organic photoreceptor) at a peripheral speed of not less than 300 mm/sec and preferably, the sleeve of the developing device at a peripheral speed exceeding the peripheral speed of the photoreceptor. The magnetic flux density on the sleeve is kept at not less than 950 gauss to prevent the developing agent being transported on the sleeve from scattering. A highly durable polycarbonate enduring such high speed copying has been selected as a binder resin to constitute the light-sensitive layer of the organic photoreceptor.

The organic photoreceptor for the method of image formation of the present invention comprises an electroconductive support and a light-sensitive layer formed thereon which contains a carrier generation material, a carrier transport material, a binder resin, and where necessary, an antioxidant, an ultraviolet absorbent and other additives, between which an interlayer is provided if necessary. The light-sensitive layer may be of a single layer structure having the above-mentioned compositions in common or of a laminated structure having a carrier generation layer based on a carrier generation material and a carrier transport layer based on a carrier transport material.

Typical structural configurations of the light-sensitive layer for the present invention are shown in Figures 1 to 6.

Figure 1 shows a photoreceptor with a laminated layer structure comprising an electroconductive support 1, a carrier generation layer 2 formed thereon and a carrier transport layer 3 formed thereon. Figure 3 shows a photoreceptor having the same layer structure as the photoreceptor of Figure 1 except that an interlayer 5 is present between the electroconductive support 1 and the carrier generation layer 2.

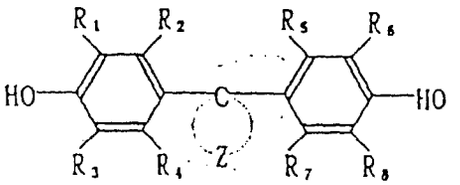
Figure 2 shows a photoreceptor with a laminated layer structure which comprises an electroconductive support 1, a carrier transport layer 3 formed thereon, a carrier generation layer formed thereon and a protective layer 8 formed on the carrier generation layer to protect it. Figure 4 shows a photoreceptor having the same layer structure as the photoreceptor of Figure 2 except that an interlayer 5 is present. Figure 5 shows a photoreceptor with a single layer structure comprising an electroconductive support 1 and a layer containing a carrier generation material 7 and a carrier transport material 6. Figure 6 is a photoreceptor having the same layer structure as the photoreceptor of Figure 5 except that an interlayer 5 is present. A key to the present invention is the use of a polycarbonate based on the repeat unit represented by Formula 1 as a binder resin in the light-sensitive layer of the photoreceptor used, whereby a highly durable photoreceptor is obtained, which ensures stable obtainment of high quality images over a long period without involving fatigue deterioration of electrophotographic properties due to severe temperature/humidity conditions, ultraviolet rays, ozone and mechanical abrasion during repeated image formation at high speed, a feature of the present invention. The polycarbonate represented by Formula 1 has been selected as suiting to the present invention from the group comprising conventional polycarbonates with various structures. The central carbon atom in the polycarbonate structure is involved in the formation of a ring by Z, which effectively prevents the molecular chain in the polycarbonate structure from orienting in a particular direction and hence prevents the crystallization and gelation of the polycarbonate. In the event of crystallization or gelation upon formation of the light-sensitive layer of photoreceptor, the resulting crystal or gel separates on, and protrudes from, the light-sensitive layer surface to cause an imaging failure.

When using the polycarbonate represented by Formula 1 to form a light-sensitive layer, it is possible to prepare an electrophotographic photoreceptor which is excellent in light-sensitive layer physical properties and electrophotographic properties such as charge retention, sensitivity and residual potential and which shows stable performance with little fatigue deterioration even in repeated use at high speed.

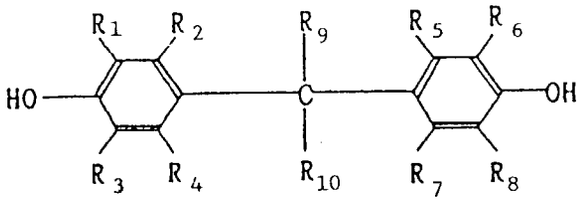
When using the photoreceptor of the method of the present invention in copying machines and other equipment

which form images at high speed, the light-sensitive layer surface is not liable to have flaws even after abrasion with a magnetic brush or a cleaning blade and a high printability free of characteristic failures such as poor cleaning is obtained.

The polycarbonate resin of the present invention can easily be synthesized by a conventional method using, for example, a phenol compound represented by the following formula.



wherein Z represents a group of non-metallic atoms necessary to complete a substituted or unsubstituted carbon ring or heterocyclic ring group; R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, chlorine atom, bromine atom or methyl group. Not all the substituents are hydrogen atoms at the same time.



wherein R_9 and R_{10} independently represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms. R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 independently represent a hydrogen atom, methyl group, chlorine atom or bromine atom. Not all the substituents are hydrogen atoms at the same time.

An example of the method of producing the polycarbonate resin for the present invention is such that the phenol compound described above is reacted with an aqueous solution of alkali, pyridine or another acid recipient in the presence of an inert solvent such as methylene chloride or 1,2-dichloroethane while introducing phosgene.

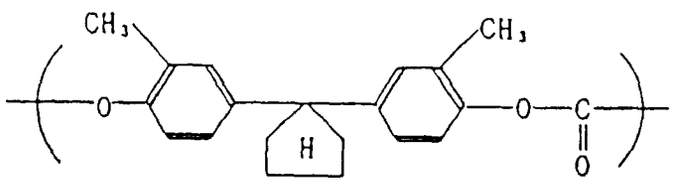
When using an aqueous solution of alkali as an acid recipient, catalytic use of a tertiary amine such as trimethylamine or triethylamine or a quaternary ammonium compound such as tetrabutylammonium chloride or benzyltributylammonium bromide increases the reaction rate.

A monohydric phenol such as phenol or p-t-butylphenol may be added as a molecular weight regulator as necessary. The catalyst may be present at initiation of the reaction, or may be added after preparing the oligomer before increasing the molecular weight.

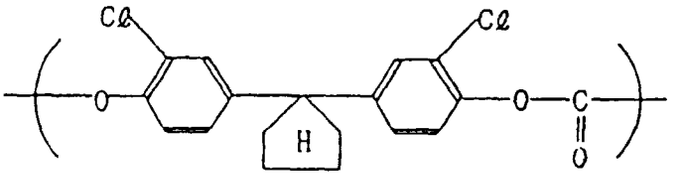
In the polycarbonate structure of Formula 1, Z forms a 5- or 6-membered carbon ring or heterocyclic ring, including a cyclohexyl ring or a cyclopentyl ring, optionally substituted by a substituent such as an acetyl group or acetylamino group.

The repeat unit compound for the polycarbonate for the present invention is exemplified as follows.

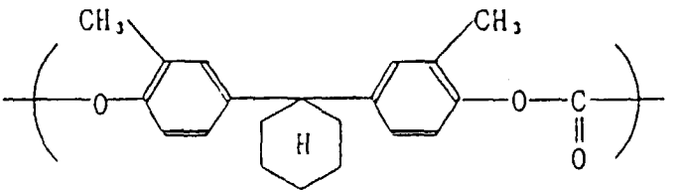
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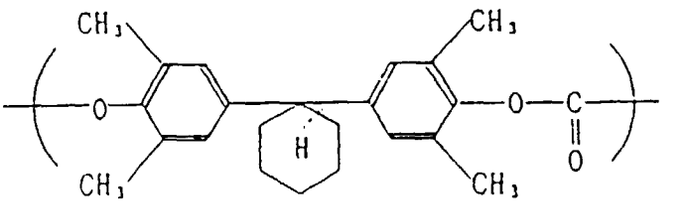
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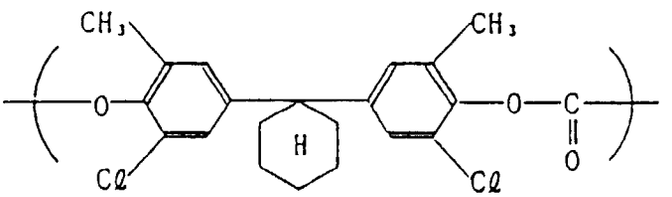
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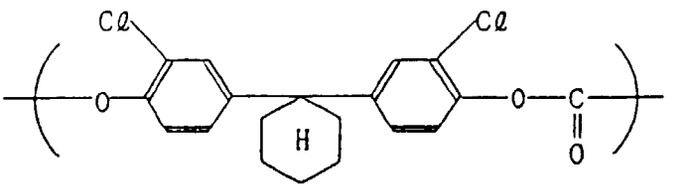
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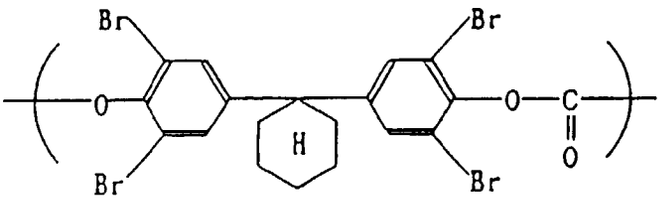
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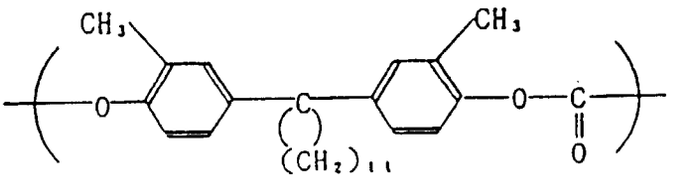
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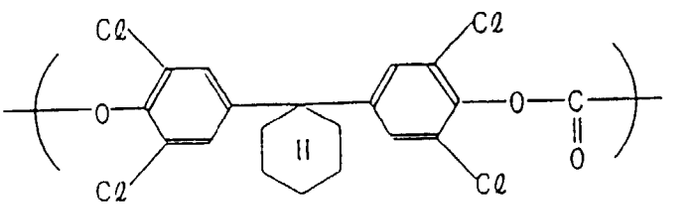
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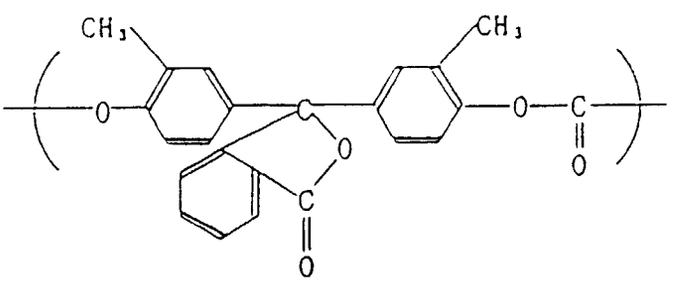
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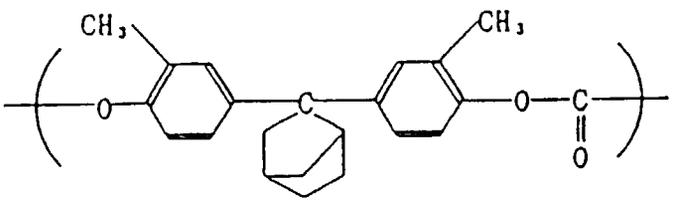
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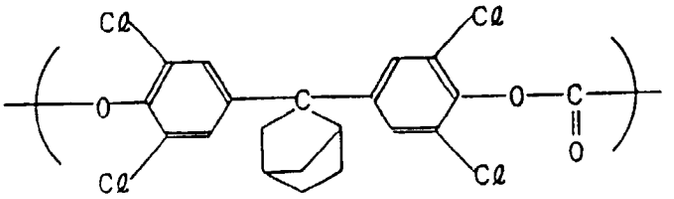
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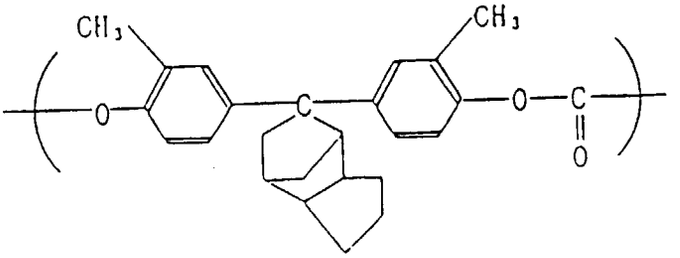
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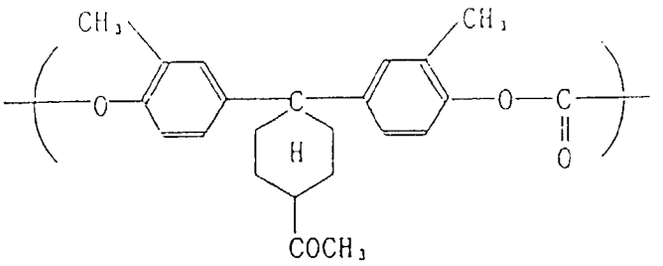
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(1)-13



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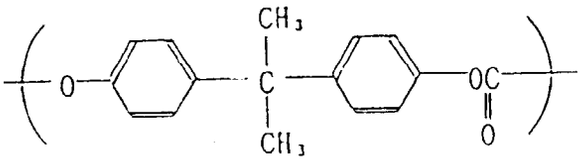


Of these compounds, (1)-3 and (1)-6 serve as repeat unit structures providing excellent mechanical durability in the polycarbonate.

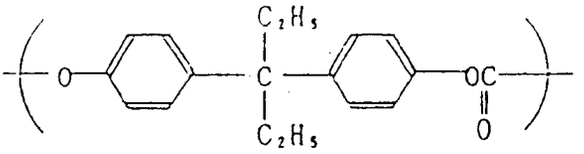
The binder resin for the photoreceptor of the present invention may be formulated with another resin, as long as its effect on the polycarbonate of Formula 1 is not interfered with, preferably at mixing ratios of not more than 50 wt%.

The polycarbonate for the present invention may be a homopolymer of a structural unit (II) represented above but may also be a copolymer with another structural unit A or B with the following structures. In this case, the mixing ratio of the other structural unit is preferably not more than 50 wt%.

Structural unit A



Structural unit B



Various methods including the following can be used to copolymerize two or more phenol compounds for the present invention.

(a) Copolymerization is carried out by simultaneously reacting two or more phenol compounds with phosgene.
(b) Copolymerization is carried out by first reacting one or more phenol compounds with phosgene and after the reaction has progressed to some extent, the remaining phenol compounds are added for further reaction.
(c) Copolymerization is carried out by separately reacting two or more phenol compounds with phosgene.

The degree of polymerization of the homopolymer or copolymer of the polycarbonate for the present invention is 50 to 5000, preferably 50 to 1000.

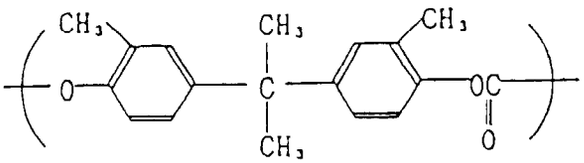
Examples of binder resins which can be used in combination with the homopolymer or copolymer of the polycarbonate include the following.

(1) Polyester
(2) Methacrylic resin
(3) Acrylic resin
(4) Polyvinyl chloride
(5) Polyvinylidene chloride
(6) Polystyrene
(7) Polyvinyl acetate
(8) Styrene copolymer resins such as styrene-butadiene copolymer and styrene-methyl methacrylate copolymer
(9) Acrylonitrile copolymer resins such as vinylidene chloride-acrylonitrile copolymer
(10) Vinyl chloride-vinyl acetate copolymer
(11) Vinyl chloride-vinyl acetate-maleic anhydride copolymer
(12) Silicone resin
(13) Silicone-alkyd resin
(14) Phenol resins such as phenol-formaldehyde resin and cresol-formaldehyde resin
(15) Styrene-alkyd resin
(16) Poly-N-vinylcarbazole
(17) Polyvinyl butyral
(18) Polyvinyl formal
(19) Polyhydroxystyrene

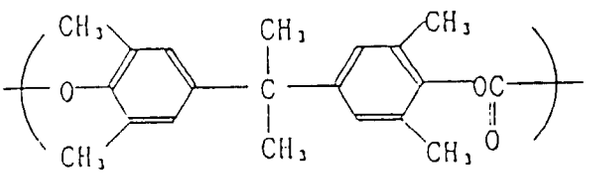
These binders may be used singly or in a mixture of two or more in combination with the polycarbonate at not more than 50 wt%.

Examples of the structural unit for polycarbonates of Formula II are as follows:

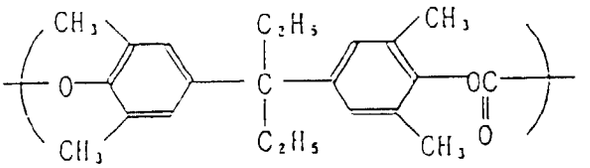
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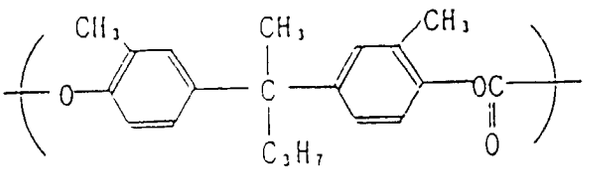
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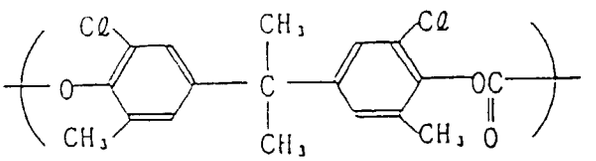
(II)-3



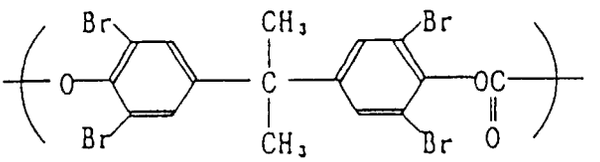
(II)-4



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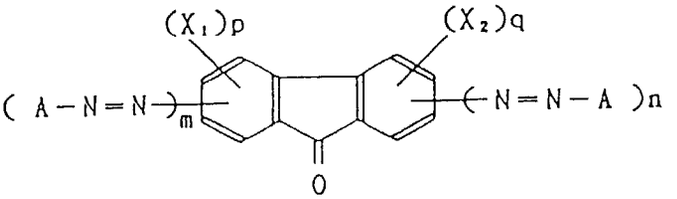
The following organic pigments, for example, are used as carrier generation materials added to the light-sensitive layer to prepare the photoreceptor of the present invention.

(1) Azo pigments such as monoazo pigments, bisazo pigments, triazo pigments and metal complex salt azo pigments.
(2) Perillene pigments such as perillic anhydride and perillic imide.
(3) Polycyclic quinone pigments such as anthraquinone derivatives, anthanthrone derivatives, dibenzopyrenequinone derivatives, pyranthrone derivatives, violanthrone derivatives and isoviolanthrone derivatives.
(4) Indigoid pigments such as indigo derivatives and thioindigo derivatives.
(5) Phthalocyanine pigments such as metallic phthalocyanines and non-metallic phthalocyanines.

It is preferable to use an organic pigment such as a fluorenone dis-azo pigment, fluorenylidene dis-azo pigment, polycyclic quinone pigment, non-metallic phthalocyanine pigment or oxytitanyl phthalocyanine pigment as a carrier generation material in the photoreceptor for the present invention, with more preference given to the following fluorenone diazo pigment, fluorenylidene dis-azo pigment, polycyclic quinone pigment and X- and τ-type non-metallic phthalocyanines, since they offer remarkable improvements in sensitivity, durability, image quality and other features.

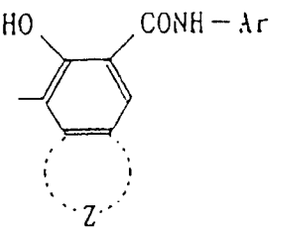
Examples of suitable pigments include the following:

Formula 2



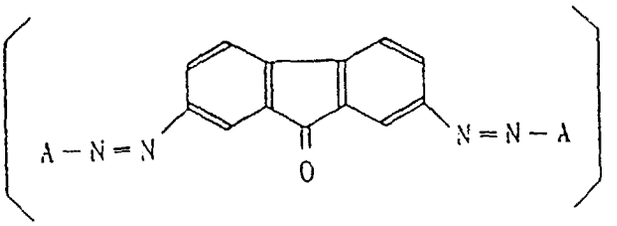
wherein X_1 and X_2 independently represent a halogen atom, alkyl group, alkoxy group, nitro group, cyano group, hydroxyl group or substituted or unsubstituted amino group; p and q independently represent 0, 1 or 2; when p and q are 2, X_1 and X_2 may be identical or not; A represents a group represented by the following Formula 2-1:

Formula 2-1



wherein Ar represents a fluorinated hydrocarbon group or an aromatic carbon ring group or aromatic heterocyclic ring having a substituent; Z represents a group of non-metallic atoms necessary to complete a substituted or unsubstituted aromatic carbon ring or substituted or unsubstituted aromatic heterocyclic ring; m and n independently represent 0, 1 or 2; m and n are not 0 at the same time.

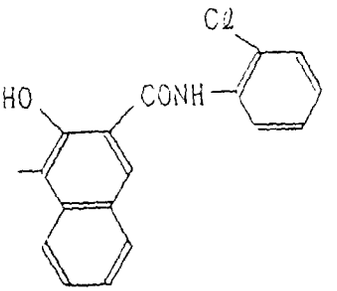
Examples of fluorenone dis-azo pigments suitable for use in the present invention are given below, but the invention is not limited by these examples.



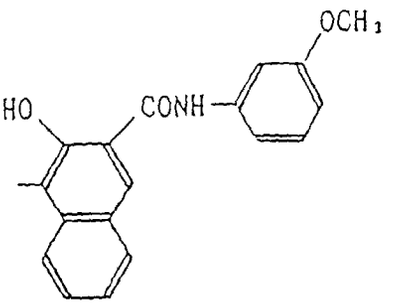
A

Compound number

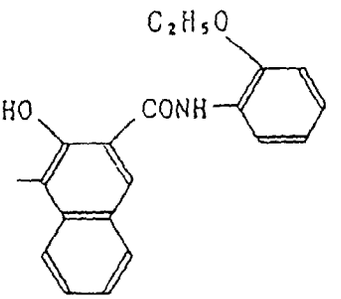
(2) - 1



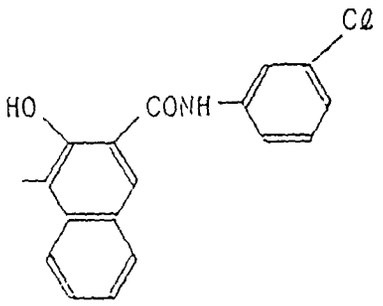
(2) - 2



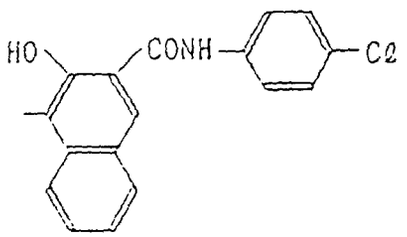
(2) - 3

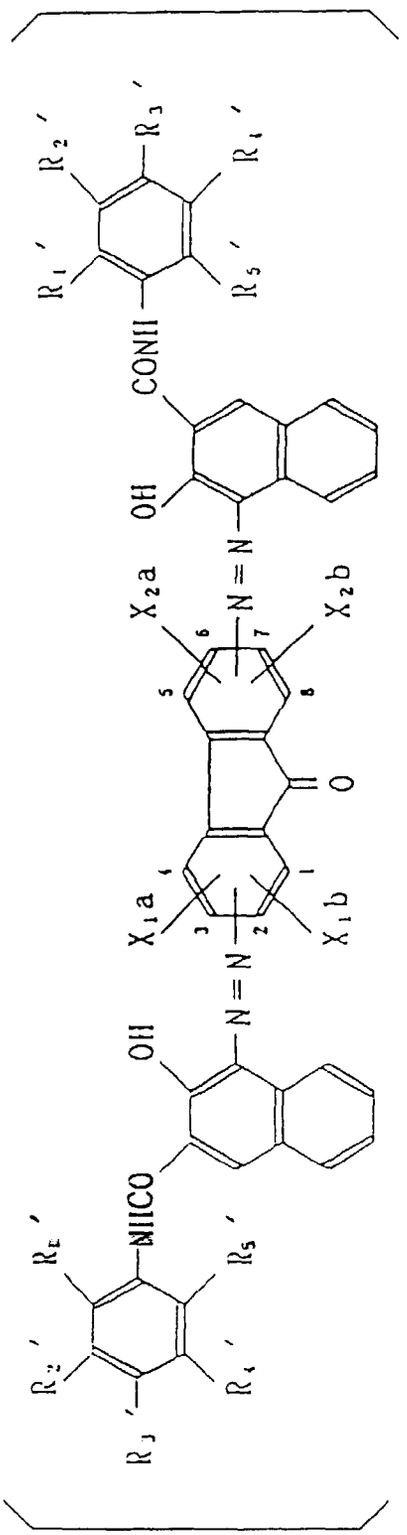


(2) - 4



(2) - 5





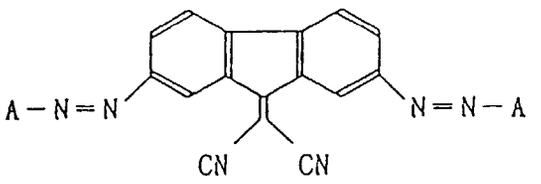
Compound number	Azo group substitution position	X_1a	X_1b	X_2a	X_2b	R_1'	R_2'	R_3'	R_4'	R_5'
(2)-6	2,7-position	4-F	H	H	H	H	CF_3	H	H	H
(2)-7	2,7-position	4-F	H	H	H	CF_3	H	H	CF_3	H
(2)-8	2,7-position	3-F	H	5-F	H	CF_3	H	H	H	H
(2)-9	2,7-position	3-F	H	6-OH	H	H	CF_3	H	H	H
(2)-10	2,7-position	4-Cl	H	H	H	H	CF_3	Cl	H	H

Compound number	Azo group substitution position	X_1a	X_1b	X_2a	X_2b	R_1'	R_2'	R_3'	R_4'	R_5'
(2)-11	2,7-position	3-Cl	H	6-Cl	H	H	CF_3	H	H	H
(2)-12	2,7-position	4-Br	H	H	H	H	CF_3	H	H	H
(2)-13	2,7-position	4-Br	H	5-Br	H	H	H	CF_3	H	H
(2)-14	2,7-position	1-Br	3-Br	6-Br	H	H	CF_3	H	H	H
(2)-15	2,7-position	4-I	H	H	H	H	CF_3	H	H	H
(2)-16	2,7-position	4-I	H	H	H	CF_3	H	H	CF_3	H
(2)-17	2,7-position	4-Cl	H	H	H	H	CF_3	H	H	H
(2)-18	2,6-position	2-Cl	H	7-Cl	H	H	CF_3	H	H	H
(2)-19	3,6-position	4-Br	H	H	H	H	H	CF_3	H	H
(2)-20	3,6-position	4-I	H	H	H	Cl	H	H	CF_3	H
(2)-21	2,5-position	3-Br	H	H	H	H	CF_3	H	H	H
(2)-22	1,8-position	3-Cl	H	H	H	H	CF_3	H	H	H
(2)-23	2,7-position	4-Br	H	H	H	H	H	H	CF_3	H
(2)-24	2,7-position	4-I	H	H	H	H	CF_3	H	H	Cl

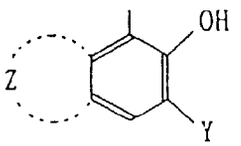
The fluorenone dis-azo pigment represented by Formula 2 useful in the present invention can easily be synthesized by a known method, for example, the method described in Japanese Patent Application No. 304862/1987.

Fluorenylidene dis-azo pigment useful in the present invention are represented by the following Formula 3.

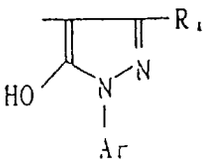
Formula 3



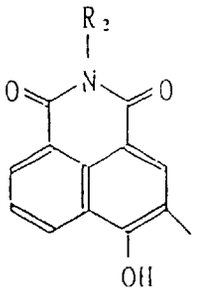
wherein A represents



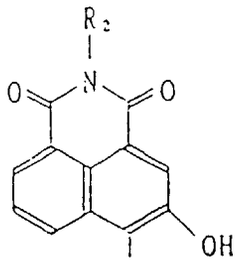
,



,



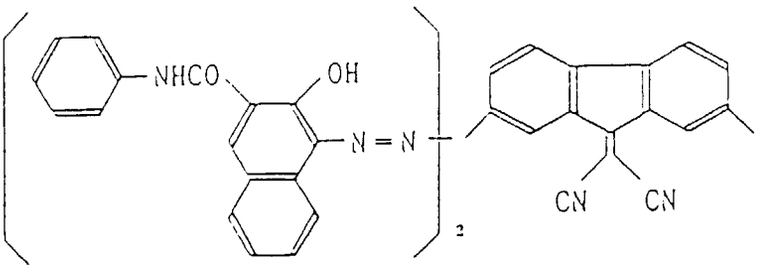
or



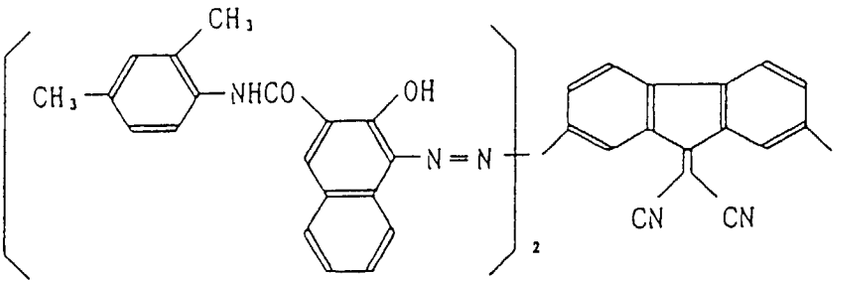
wherein Z represents a group of atoms necessary to complete a substituted or unsubstituted aromatic carbon ring or aromatic heterocyclic ring group; Y represents a hydrogen atom, hydroxyl group, carboxyl group or its ester, sulfo group, substituted or unsubstituted carbamoyl group or sulfamoyl group; R_1 represents a hydrogen atom, a substituted or unsubstituted alkyl group, amino group, carbamoyl group or carboxyl group or its ester or a cyano group; Ar represents a substituted or unsubstituted aryl group; R_2 represents a substituted or unsubstituted alkyl group, aralkyl group or aryl group.

Examples of dis-azo pigments of Formula 3 which may be used in the present invention are provided below, but are not to be construed as limitative.

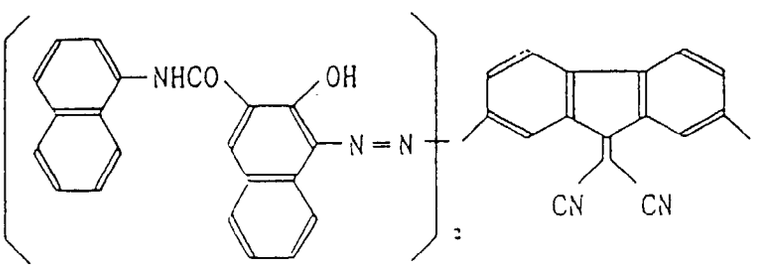
(3) - 1



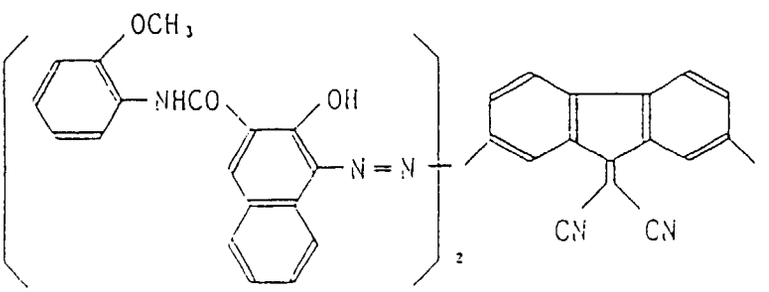
(3) - 2



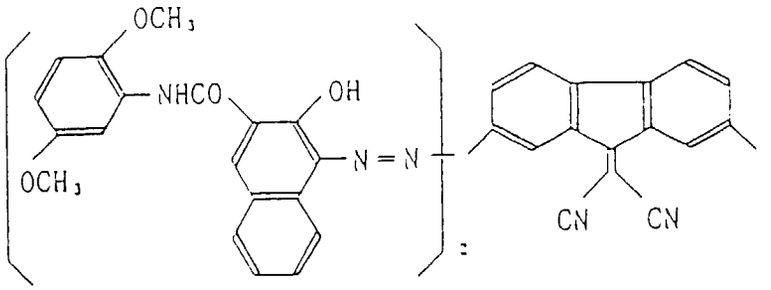
(3) - 3



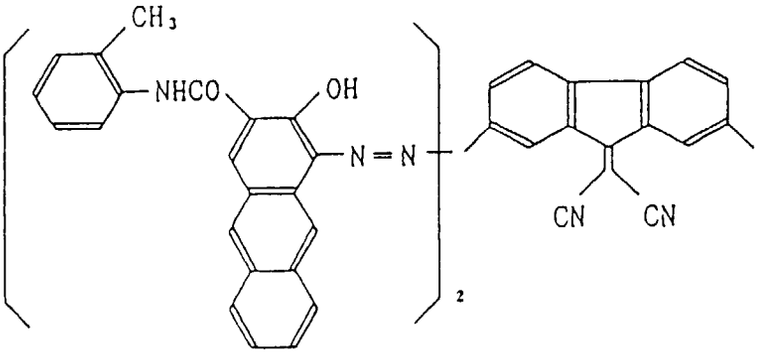
(3) - 4



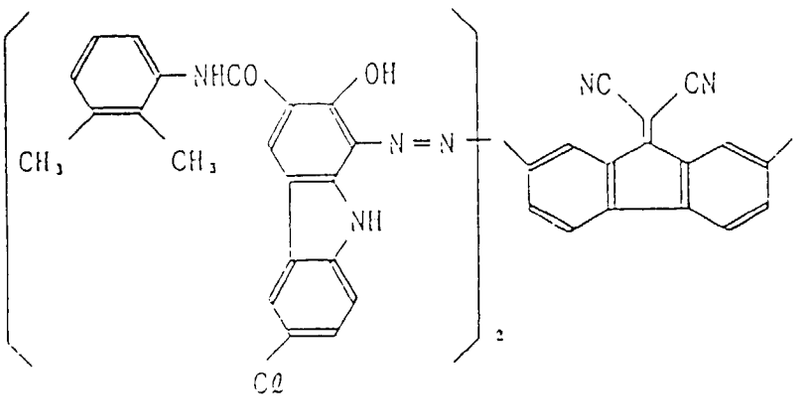
(3) - 5


OCH3
NHCO
OH
N=N
OCH3
CN
CN
2

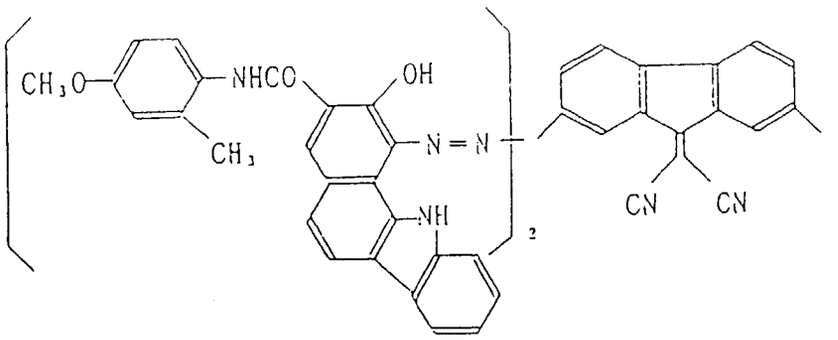
(3) - 6


CH3
NHCO
OH
N=N
CN
CN
2

(3) - 7

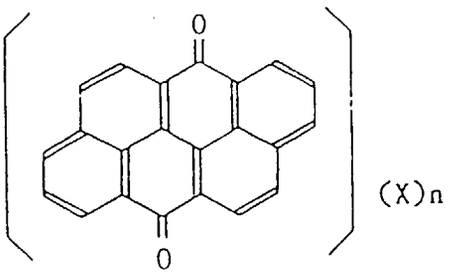

NHCO
OH
CH3
CH3
N=N
NH
Cℓ
NC
CN
2

(3) - S

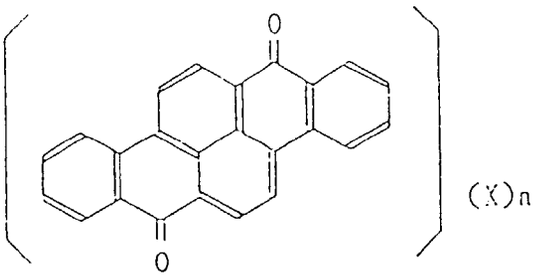


Examples of polycyclic quinone pigments suitable for use in the present invention are represented by the following Formulae 4 to 6 below:

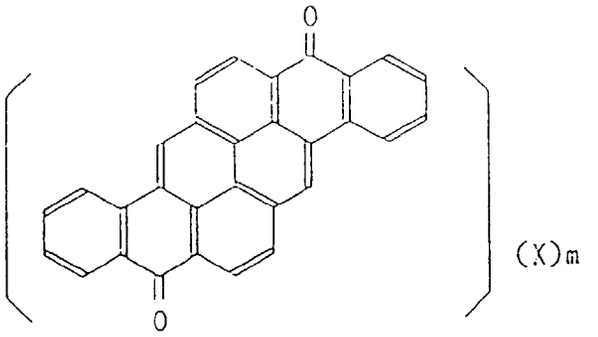
Formula 4



Formula 5



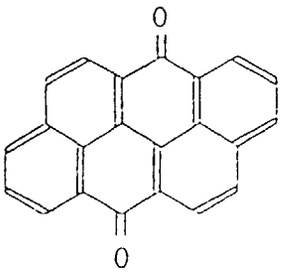
Formula 6



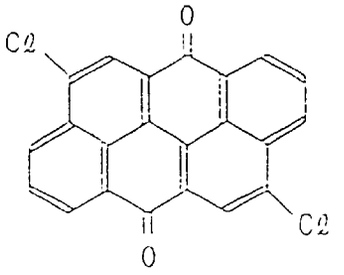
wherein X represents a halogen atom, nitro group, cyano group, acyl group or carboxyl group; n represents 0 to 4; m represents 0 to 6.

Examples of polycyclic quinone pigments of Formulae 4 to 6 suitable for use in the present invention are given below, but the invention is not limited by these examples:

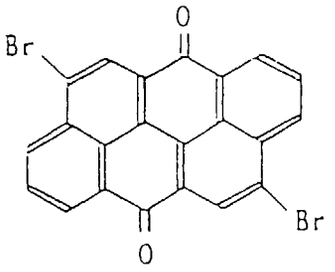
(4) - 1



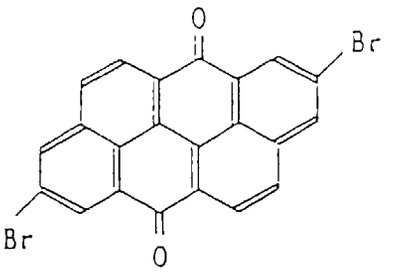
(4) - 2



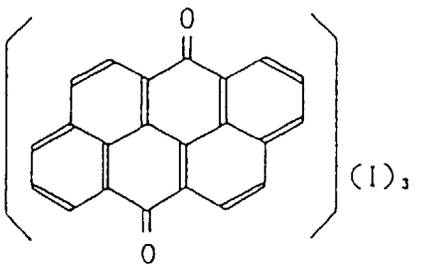
(4) - 3



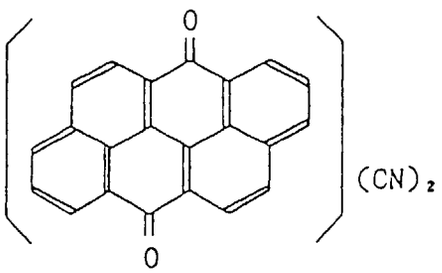
(4) - 4



(4) - 5

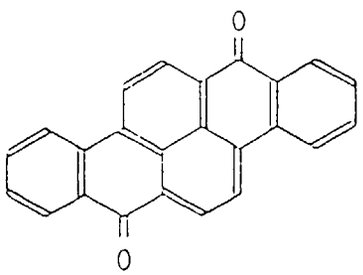


(4) - 6

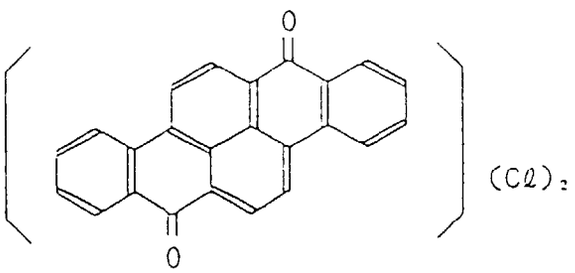


The dibenzopyrenequinone pigment represented by Formula 5 is exemplified by the following compounds.

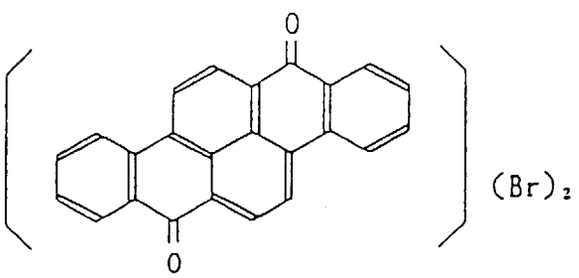
(5) - 1



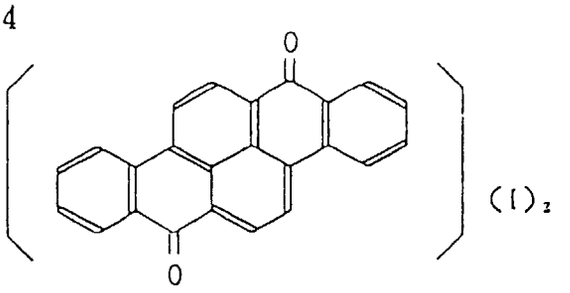
(5) - 2



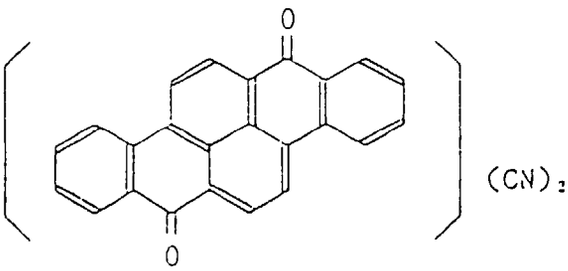
(5) - 3



(5) - 4

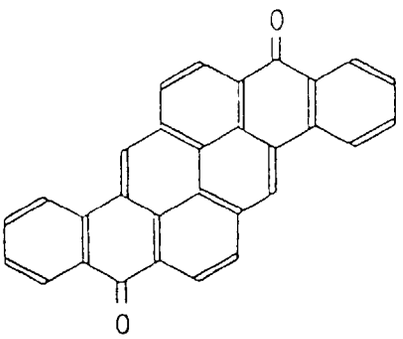


(5) - 5

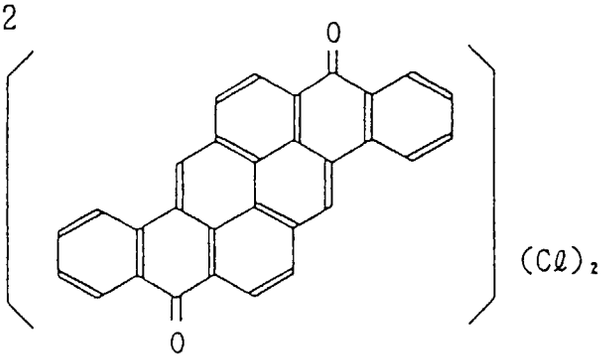


The pyranthrone pigment represented by Formula 6 is exemplified by the following compounds.

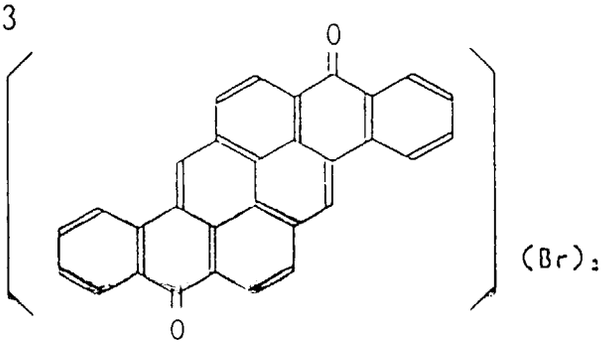
(6) - 1



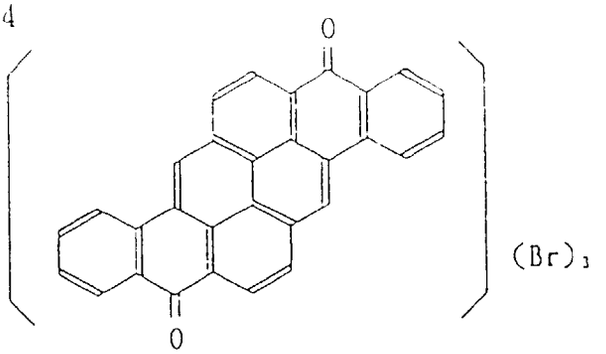
(6) - 2



(6) - 3



(6) - 4



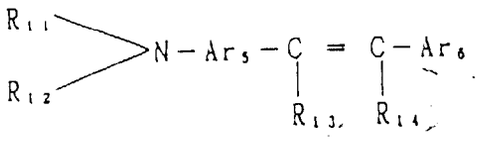
The polycyclic quinones represented by Formulae 4 to 6 suitable for use in the present invention can easily be synthesized by known methods.

Any non-metallic phthalocyanine and its derivative can be used for the present invention, as long as it is electroconductive. Examples thereof include those of the α-type, β-type, τ,τ'-type, η,η'-type, X-type and crystal configuration described in Japanese Patent O.P.I. Publication No. 103651/1987 and derivatives thereof. It is desirable to use the τ-, X- or K/R-X type. Non-metallic phthalocyanines of the X-type are described in U.S. Patent No. 3,357,989. Non-metallic phthalocyanines of the τ-type are described in Japanese Patent O.P.I. Publication No. 182639/1983. The phthalocyanines of the K/R-X type are characterized in that major peaks appear at 7.7, 9.2, 16.8, 17.5, 22.4 and 28.8° as of Brag angle (2θ ±0.2°) with respect to the X-ray from CuK_2 of 1.541 Å with the ratio of the 16.8° peak intensity to the 9.2° peak intensity ranging from 0.8 to 1.0 and the ratio of the 28.8° peak intensity to the 22.4° peak intensity exceeding 0.4, as described in Japanese Patent O.P.I. Publication No. 103651/1987.

There is no limitation on the choice of carrier transport materials for the present invention. Examples of usable carrier transport materials include oxazole derivatives, oxadiazole derivatives, thiazole derivatives, thiadiazole derivatives, triazole derivatives, imidazole derivatives, imidazolone derivatives, imidazolidine derivatives, bisimidazolidine derivatives, styryl compounds, hydrazone compounds, pyrazoline derivatives, amine derivatives, oxazolone derivatives, benzothiazole derivatives, benzimidazole derivatives, quinazoline derivatives, benzofuran derivatives, acridine derivatives, phenazine derivatives, aminostilbene derivatives, poly-N-vinylcarbazole, poly-1-vinylpyrene and poly-9-vinylanthracene.

The carrier transport material for the present invention is preferably a carrier transport material which is highly capable of transporting the holes which result from light irradiation to the support side and which is suitable for combined use with the organic pigment. Such carrier transport materials are exemplified by the styryl compounds represented by the following Formulas 7 and 8.

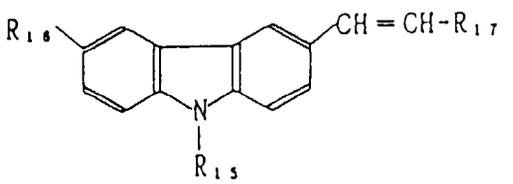
Formula 7



wherein R_{11} and R_{12} independently represent a substituted or unsubstituted alkyl group or aryl group, the substituent being exemplified by an alkyl group, alkoxy group, substituted amino group, hydroxyl group, halogen atom and aryl group. Ar_5 and Ar_6 independently represent a substituted or unsubstituted aryl group, the substituent being exemplified by an alkyl group, alkoxy group, substituted amino group, hydroxyl group, halogen atom and aryl group. R_{13} and R_{14} independently represent a substituted or unsubstituted aryl group or hydrogen atom, the substituent being exemplified by an alkyl group, alkoxy group, substituted amino group, hydroxyl group, halogen atom and aryl group.

Compounds represented by Formula 7 are described in Japanese Patent O.P.I. Publication Nos. 65440/1983, 198425/1983, 198043/1983, 93445/1985 and 98437/1985 and other publications.

Formula 8

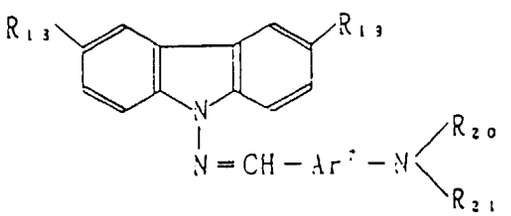


wherein R_{15} represents a substituted or unsubstituted aryl group; R_{16} represents a hydrogen atom, halogen atom, substituted or unsubstituted alkyl group, alkoxy group, amino group, substituted amino group or hydroxyl group; R_{17} represents a substituted or unsubstituted aryl group or heterocyclic group.

Compounds represented by Formula 8 are described in Japanese Patent O.P.I. Publication No. 148750/1982 and other publications.

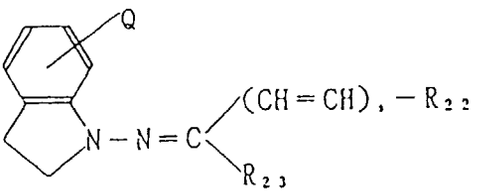
The hydrazone compounds of the following Formulas 9 through 11 can also be used as carrier transport materials.

Formula 9

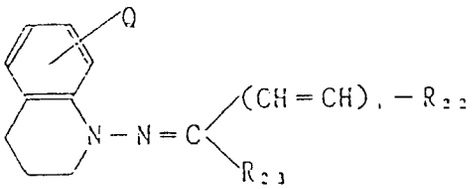


wherein R_{18} and R_{19} independently represent a hydrogen atom or halogen atom; R_{20} and R_{21} independently represent a substituted or unsubstituted aryl group; Ar^7 represents a substituted or unsubstituted arylene group. Compounds represented by Formula 9 are described in Japanese Patent O.P.I. Publication No. 72148/1982 and other publications.

Formula 10



Formula 11

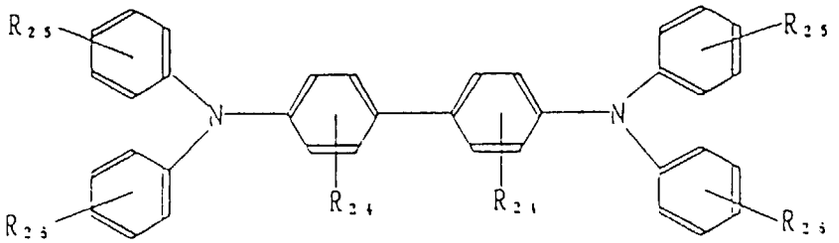


wherein R_{22} represents a substituted or unsubstituted aryl group or heterocyclic group; R_{23} represents a hydrogen atom or a substituted or unsubstituted aralkyl group or aryl group; Q represents a hydrogen atom, halogen atom, alkyl group, substituted amino group, alkoxy group or cyano group; S represents 0 or 1.

Compounds represented by Formulae 10 and 11 are described in Japanese Patent O.P.I. Publication Nos. 134642/1983 and 166354/1983 and other publications.

The tetraphenylbenzidine compound of Formula 12 can also be used as a carrier transport material.

Formula 12

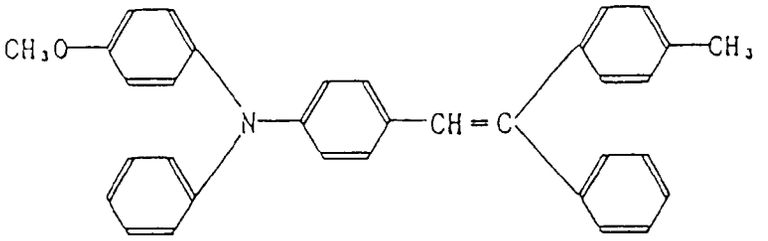


wherein R_{24} and R_{25} independently represent a hydrogen atom or methyl group; R_{26} represents a hydrogen atom, methyl group, ethyl group or chlorine atom.

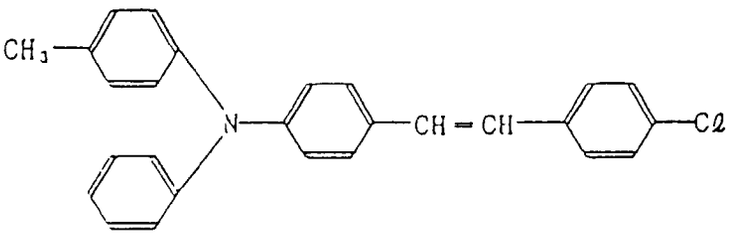
Examples of other useful carrier transport materials include those described in Japanese Patent O.P.I. Publication Nos. 64244/1982, 15252/1984, 67940/1982, 2285/1980, 195254/1982 and 4148/1981.

Compounds which serve very well as carrier transport materials in the photoreceptor used for the method of image formation of the present invention are exemplified below.

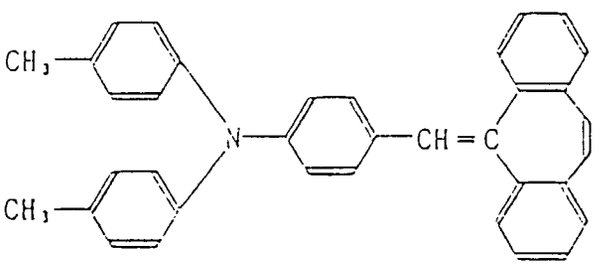
(7) - 1



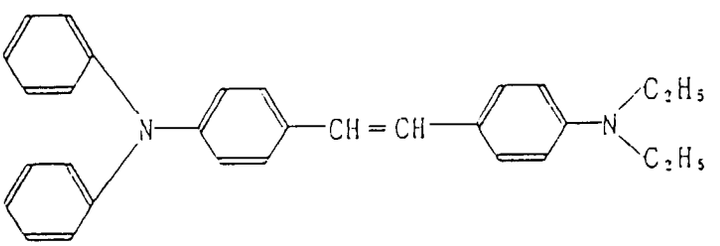
(7) - 2



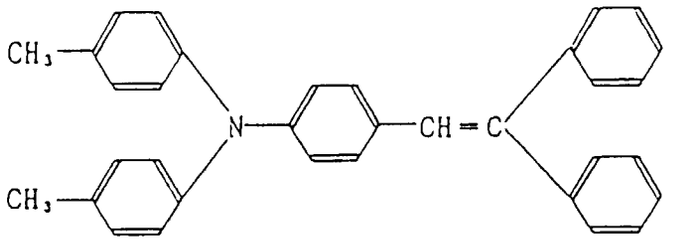
(7) - 3



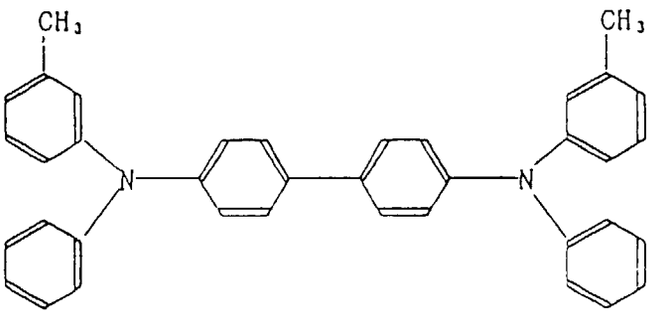
(7) - 4



(7)-5



(12)-1



Examples of the dispersant or solvent used to disperse the carrier generation material or dissolve the carrier transport material and binder resin in the formation of the light-sensitive layer of the photoreceptor of the present invention include hydrocarbons such as hexane, benzene, toluene and xylene, halogenated hydrocarbons such as methylene chloride, methylene bromide, 1,2-dichloroethane, syn-tetrachloroethane, cis-1,2-dichloroethylene, 1,1,2-trichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, chloroform, bromoform and chlorobenzene, ketones such as acetone, methyl ethyl ketone and cyclohexanone, esters such as ethyl acetate and butyl acetate, alcohols such as methanol, ethanol, propanol, butanol, cyclohexanol, heptanol, ethylene glycol, methyl cellosolve, ethyl cellosolve, acetyl cellosolve and derivatives thereof, ethers or acetals such as tetrahydrofuran, 1,4-dioxane, furan and furfural, nitrogen compounds such as pyridine, butylamine, diethylamine, ethylenediamine, isopropanolamine and other amines and N,N-dimethylformamide and other amides, fatty acids, phenols and sulfur or phosphorus compounds such as carbon disulfide and triethyl phosphate.

In the present invention, for improving the sensitivity, reducing the residual potential and the fatigue during repeated use and other purposes, the light-sensitive layer may contain one or more electron recipient substances.

Examples of electron recipients which can be used for these purposes include succinic anhydride, maleic anhydride, dibromomaleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, 3-nitrophthalic anhydride, 4-nitrophthalic anhydride, pyromellitic anhydride, mellitic anhydride, tetracyanoethylene, tetracyanoquinodimethane, o-dinitrobenzene, m-dinitrobenzene, 1,3,5-trinitrolbenzene, p-nitrobenzonitrile, picryl chloride, quinone chlorimide, chloranil, bromanil, dichlorodicyanoparabenzoquinone, anthraquinone, dinitroanthraquinone, 2,7-dinitrofluorenone, 2,4,7-trinitrofluorenone, 2,4,5,7-tetranitrofluorenone, 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 highly electrophilic compounds. The ratio of electron recipient added is 0.01 to 200 parts by weight, preferably 0.1 to 100 parts by weight to 100 parts by weight of the organic pigment used as a carrier generation material for the invention.

The light-sensitive layer for the present invention may contain an organic amine to improve the charge generation function of the carrier generation material, with preference given to a secondary amine. Such compounds are described in Japanese Patent O.P.I. Publication Nos. 218447/1984 and 8160/1987.

The photoreceptor for the present invention may contain as necessary an ultraviolet absorbent and other additives to protect the light-sensitive layer and also a color sensitivity correcting dye.

The protective layer 8 shown in Figure 2 or 4 may contain as necessary a thermoplastic resin at concentrations below 50 for the purpose of improving the processability and physical properties, for example, to prevent cracking and

providing flexibility.

The interlayer 5 shown in Figure 3, 4 or 6 functions as an adhesive layer, blocking layer or another layer, which may comprise polyvinyl alcohol, ethyl cellulose, carboxymethyl cellulose, vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinyl acetate-maleic anhydride copolymer, casein, N-alkoxymethylated nylon, starch and other substances as well as ordinary binder resins.

The electroconductive support 1 which constitutes the photoreceptor for the present invention is prepared mainly from the following substances, but these are not to be construed as limitative.

1) Metal plates such as aluminum and stainless steel plates.
2) Paper or plastic film supports on which a thin layer of a metal such as aluminum, palladium or gold has been formed by lamination or evaporative deposition.
3) Paper or plastic film supports on which a layer of an electroconductive compound such as electroconductive polymer, indium oxide or tin oxide has been formed by coating or evaporative deposition.

The light-sensitive layer 4 of the photoreceptor may be of a double layer structure as illustrated in Figures 1 through 4 or of a single layer structure as illustrated in Figures 5 and 6. In the case of double layer structure, it depends on the charging polarity, positive or negative, which of the carrier generation layer 2 or carrier transport layer 3 is located on the counterpart layer. To obtain a negatively charged photoreceptor, it is advantageous to locate the carrier transport layer 3 on the carrier generation layer 2. To obtain a positively charged photoreceptor, it is advantageous to locate the carrier generation layer 2 on the carrier transport layer 3. This is because the carrier transport material in the carrier transport layer 3 is highly capable of transporting positive holes. A photoreceptor having a light-sensitive layer 4 of a double layer structure described above is prepared by the following methods.

(1) Vacuum deposition.
(2) Coating a solution of carrier transport material in an appropriate solvent.
(3) Coating a dispersion prepared by finely pulverizing a carrier transport material using a ball mill, sand grinder or another means in a dispersant and if necessary mixing and dispersing with a binder.

Specifically, there can be used vapor phase deposition methods such as vacuum deposition, sputtering and CVD and coating methods such as dip coating, spray coating, blade coating and roll coating.

The thickness of the carrier generation layer 2 thus formed is preferably 0.01 to 5 μm, more preferably 0.05 to 3 μm. The carrier generation layer 2 is a layer wherein fine particles of carrier generation material typically having a diameter of not more than 1 μm as a main component is dispersed in a binder resin in a ratio of 0.1 to 3 parts by weight of the binder resin to 1 part by weight of the carrier generation material.

The carrier generation layer 2 may contain as necessary a carrier transport material at 0 to 1 part by weight.

The carrier transport layer 3 is a layer wherein a carrier transport material as a main component is compatibly dissolved in a binder resin in a ratio of 0.1 to 5 parts by weight of the binder resin to 1 part by weight of the carrier transport material. The light-sensitive layer 4 of the photoreceptor for the present invention may be of a single layer structure. In this case, the thickness of the light-sensitive layer is 10 to 50 μm, preferably 15 to 40 μm, wherein 0.5 to 5 parts by weight of the carrier transport material and 0.5 to 10 parts by weight of the binder resin are contained per 1 part by weight of the carrier generation material.

With the structure described above, the photoreceptor for the present invention offers excellent electrophotographic performance with high durability and little fatigue deterioration when used for high speed repetitive transfer electrophotography.

Developers suitable for the present invention are described below. The developer used for the present invention is a two-component developer which is excellent in fluidity and frictional chargeability and hence in developability. The two-component developer preferably comprises a fine grains of non-magnetic toner and magnetic carrier grains.

To obtain such fine grains of non-magnetic toner, a colorant such as carbon black in a ratio of not more than 20 wt% and, where necessary, a charge control agent in a ratio of not more than 5 wt%, are added to the thermoplastic or thermosetting resin described below, followed by melting, kneading, cooling, pulverization and classification, and if necessary heat treatment to yield insulating grains having a volume resistivity of not less than 10^{14} Ω-cm and a weight average grain size of 2 to 20 μm. A binder resin monomer containing the colorant and other additives may be polymerized while stirring to yield a spherical toner.

Examples of the binder resin to prepare the toner include addition polymerization resins such as styrene resin, styrene-acrylic resin, styrene-butadiene resin and acrylic resin, condensation polymerization resins such as polyester resin, polycarbonate resin, polyamide resin, polysulfonate resin and polyurethane resin, and epoxy resin.

Examples of the monomer used to form an addition polymerization resin include styrenes such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene and 3,4-dichlorostyrene, ethylenic unsaturated monoolefins such as

ethylene, propylene, butylene and isobutylene, halogenated vinyls such as vinyl chloride, vinylidene chloride, vinyl bromide and vinyl fluoride, vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate and vinyl acetate, α-methylene aliphatic monocarboxylates such as methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, propyl acrylate, octyl acrylate, dodecyl acrylate, lauryl acrylate, 2-ethylhexyl acrylate, octyl methacrylate, dodecyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate, acrylic acid or methacrylic acid derivatives such as acrylonitrile, methacrylonitrile and acrylamide, vinyl ethers such as vinylmethyl ether, vinylethyl ether and vinylisobutyl ether, vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone and methyl isopropenyl ketone, N-vinyl compounds such as N-vinylpyrrole, N-vinylcarbazole, N-vinylindole and N-vinylpyrrolidone, monoolefinic monomers such as vinylnaphthalenes, and diolefinic monomers such as propadiene, butadiene, isoprene, chloroprene, pentadiene and hexadiene. These monomers may be used singly or in combination. Examples of the monomer used to form a condensation polymerization resin include ethylene glycol, triethylene glycol and 1,3-propylene glycol.

As for charge control agents, all of the negative charge control agents described in Japanese Patent O.P.I. Publication Nos. 88743/1984, 88745/1984, 79256/1984, 78362/1984, 228259/1984 and 124344/1984 and all of the positive charge control agents described in Japanese Patent O.P.I. Publication Nos. 9456/1976, 204851/1984, 204850/1984 and 177571/1984 can be used.

For the purpose of preventing the offset phenomenon due to toner adherence to fixation roller, a low molecular polyolefin such as polypropylene, polyethylene or wax may be added to binder resin at 0 to 5 wt%.

For the purpose of providing fluidity and other charge control properties (negative) for the developer, hydrophobic silica may be externally added to the toner at 0 to 3 wt%.

The carrier for the two-component developer for the present invention is capable of providing the desired charge for the toner. A magnetic material may be used as such, used after being coated with resin etc. or used as fine powder in mixture with resin, with preference given to a coated carrier prepared by coating a resin on the magnetic grain surface. Examples of the magnetic material include substances which magnetize very strongly in the direction of magnetic field, such as iron, cobalt, nickel and other metals, ferrite, magnetite, hematite and other alloys or compounds containing a ferromagnetic element such as iron, cobalt or nickel, and alloys which contain no ferromagnetic substance but which show ferromagnetism upon appropriate heat treatment such as Heusler's alloys containing manganese and copper (manganese-copper-aluminum alloy and manganese-copper-tin alloy) and chromium dioxide.

The weight average grain diameter d of the carrier is normally 40 to 120 μm. The carrier resistivity is not less than 10^3 Ω-cm, preferably not less than 10^{13} Ω-cm, and still more preferably not less than 10^{14} Ω-cm for preventing charge injection into the carrier by bias voltage and subsequent adherence of the carrier on the image formation surface and leakage of bias voltage leading to elimination of the latent image charge.

The specific resistivity of carrier or toner is determined by tapping the subject grains in a container having a cross sectional area of 0.5 cm^2, then exerting a load of 1 kg/cm^3 on the tapped grains, applying a voltage such that a 10^2 to 10^5 V/cm electric field appears between the loaded grains and the bottom electrode, reading the value for current and making a given calculation. The thickness of the carrier or toner grain layer is about 1 mm.

The carrier for the present invention is preferably made spherical to improve the frictional chargeability between the carrier and the toner as well as to improve the developer fluidity and to make blocking among the carrier grains or between the carrier and the toner unlikely to occur. To obtain such a spherical carrier, a thermoplastic or thermosetting resin, for example, is coated to a thickness of 0.1 to 2 μm (0.5 to 5 wt% relative to the carrier weight) on magnetic grains previously made spherical for a resin-coated carrier, or dispersed grains prepared by dispersing a fine ferromagnetic power in resin at 30 to 70 wt% may be heated to make them spherical or subjected to spray drying to directly prepare spherical grains.

The two-component developer contains the carrier and toner in weight ratios of 98:2 to 85:15 and may contain as necessary a fluidizing agent such as hydrophobic silica, colloidal silica or silicon varnish and a cleaning aid such as a metal salt of fatty acid or fluorine surfactant in a ratio of 0.1 to 3 wt% of the toner.

The developer for use in the present invention has been described above. The method of image formation using the photoreceptor and developer described above is explained below with reference to the image forming apparatus illustrated in Figure 7. The numerical symbols in Figure 7 denote an original 10 placed on an original table 11, exposure lamps 12 and 13, reflective mirrors 14a, 14b, 14c and 14d and an image forming lens 15, a charger 16, a developing apparatus 17, a sleeve 17a rotating in the direction of the arrow, an immobilized magnet 17b having a main developing magnetic pole 17d, a hopper 17c for supplying the toner T, a stirrer 18 for developer D, a highly durable organic photoreceptor drum 20, a cleaning apparatus 21, a blade 21a housed in the cleaning apparatus 21, a power source 22 to apply a DC bias voltage to the developing sleeve 17a, a paper feed cassette 23, a paper feed roller 24, a resist roller 25, a transfer pole 28, a separation pole 29, a transfer paper transport apparatus 26, a fixation roller 27, a discharge roller 28 and a paper receiving tray 29, respectively.

First, the original 10 on the original table 11 is scanned at a speed of X in the direction of the arrow by the exposure system comprising the exposure lamps 12 and 13 and the reflective mirror 14a, from which scanning light is reflected

by the V mirrors 14b and 14c running at a speed of X/2 and which reaches the photoreceptor drum 20, pre-charged to 400 to 800 V by the charger 16 and rotating at a peripheral speed of not less than 300 mm/sec in the direction of the arrow, via the image forming lens 15 and the reflective mirror 14d, on which photoreceptor drum imagewise exposure occurs and an electrostatic latent image forms. The resulting electrostatic latent image is sled and developed by a magnetic brush developing device 17 containing a single-component developer based on a magnetic toner, or a two-component developer preferably comprising a magnetic carrier and a non-magnetic toner to form a toner image. Then, the developer D in the developing device 17 is thoroughly stirred, mixed and slid and hence charged with the toner T supplied via a toner supplying mechanism such as the hopper 17c by the stirrer 18, after which it is magnetically adsorbed to the sleeve 17a and then transported to the developing zone for developing the electrostatic latent image.

Rotating the sleeve 17a at too high a peripheral speed even in a high speed copying machine results in an excess torque, which is undesirable from the viewpoint of mechanism. To obtain high image quality, the peripheral speed of the sleeve 17a is set at 1 to 5 times the peripheral speed of the photoreceptor drum 20 (peripheral speed ratio K); therefore, as the copying speed increases, the peripheral speed of the sleeve 17a increases and carrier scattering becomes more likely to occur. In the method of image formation of the present invention, the magnetic flux density on the sleeve is at least 950 gauss, preferably not more than 1200 gauss to ensure development free of carrier scattering. If the magnetic flux density exceeds 1200 gauss, the iron powder grains mingled in the developer stand up as if they are magnetically attracted and cause abrasive deterioration of the surface of the photoreceptor during repeated image formation even when the photoreceptor has been improved according to the present invention.

Accordingly, in order to prevent the carrier scattering under a magnetic flux density of less than 1200 gauss, the peripheral speed of the photoreceptor preferably be under 600 mm/sec.

In the method of image formation of the present invention, the peripheral speed ratio K is set at a lower level to avoid an excessive peripheral speed of the sleeve 17a and magnetic flux density on the sleeve as the copying speed increases. However, the peripheral speed ratio K should be not less than 1 to maintain imaging performance, and the magnetic flux density on the sleeve must be not less than 950 gauss to prevent carrier scattering.

The toner image obtained by development as above is transferred by the transfer pole 28 onto transfer paper transported from the paper feed cassette 23 to the developing zone via the paper feed roller 24 and resist roller 25 in synchronization with image formation and then transferred by the action of the separating pole 29. The transfer paper carrying the toner image is transported by the transport means 26 to the fixing device 27, wherein it is fixed, after which it is discharged to the paper receiving tray 29 via the paper discharge roller 28.

The method of image formation described above makes it possible to stably form a high quality image at high speed.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following examples, but the invention is not limited by these examples.

In the examples given below, a carrier generation material, carrier transport material, carrier generation layer and carrier transport layer are abbreviated CGM, CTM, CGL and CTL, respectively.

Examples

Preparation of inventive photoreceptor 1

30 g of a copolymer polyamide having a 1:1:1 monomer composition comprising -amino-caproic acid, adipic acid and N-(β-aminoethyl)piperazine was added to, and dissolved in, 800 mℓ of 50°C-heated methanol (produced by Kanto Chemical Co., Ltd., EL grade) while stirring the methanol. After cooling to room temperature, 200 mℓ of 1-butanol ((produced by Kanto Chemical Co., Ltd., special grade) was added. Then, the solution was dip-coated on an aluminum drum of 100 mm in diameter to form a 0.5 μm thick interlayer.

Next, 20 g of a fluorenone dis-azo pigment (Exemplified Compound 2-23) as CGM and 10 g of a polyvinyl butyral resin S-LEC BX-1 (produced by Sekisui Chemical Co., Ltd.) as a binder were dissolved in 1000 mℓ of methyl ethyl ketone (produced by Kanto Chemical Co., Ltd., EL grade), followed by 24 hours of milling using a sand mill to yield a CGL coating solution, which was dip-coated on the interlayer to form a 0.3 μm thick CGL. Then, 120 g of a styryl compound (Exemplified Compound 7-1) and 165 g of a polycarbonate (molecular weight 22000) comprising a homopolymer of the repeat unit of Exemplified Compound 1-1 were dissolved in 1000 mℓ of 1,2-dichloroethane (produced by Kanto Chemical Co., Ltd., special grade) to yield a CTL coating solution, which was dip-coated on the CGL, followed by drying at 100°C for 1 hour to yield a 20 μm thick CTL. A photoreceptor 1 comprising sequentially laminated interlayer, CGL and CTL was thus prepared.

Preparation of inventive photoreceptor 2

A photoreceptor 2 was prepared in the same manner as in Preparation of inventive photoreceptor 1, except that the polycarbonate was replaced with a polymer comprising a homopolymer of the repeat unit of Exemplified Compound 1-2 and the CTM was Exemplified Compound 7-3.

Preparation of inventive photoreceptor 3

An interlayer was formed in the same manner as in Preparation of inventive photoreceptor 1, 20 g of a polycyclic quinone pigment (Exemplified Compound 4-3) as CGM and 10 g of a polycarbonate resin L-1250 (produced by Teijin Chemicals Ltd.) as a binder were dissolved in 1,2-dichloroethane (produced by Kanto Chemical Co., Ltd., special grade), followed by 24 hours of milling in a ball mill to yield a CGL coating solution, which was dip-coated on the interlayer to yield a 0.3 μm thick CGL.

Then, a photoreceptor 3 was prepared by CTL lamination in the same manner as in Preparation of inventive photoreceptor 1, except that the CTM was Exemplified Compound 7-5 and the binder resin was replaced with a polycarbonate (molecular weight 20000) comprising a homopolymer of the repeat unit of Exemplified Compound 1-3.

Preparation of inventive photoreceptor 4

12 g of a polyvinyl butyral resin (S-LEC BX-1, produced by Sekisui Chemical Co., Ltd.) was dissolved in 1000 mℓ of methyl ethyl ketone. To this solution were added 5.7 g of Exemplified Compound 4-3 and 0.3 g of Exemplified Compound 2-23 as CGM, followed by dispersion using a sand grinder for 10 hours.

The resulting dispersion was dip-coated on the interlayer described in Preparation of inventive photoreceptor 1 to yield a CGL, followed by CTL formation in the same manner as photoreceptor 2 to yield a photoreceptor 4.

Preparation of inventive photoreceptor 5

A photoreceptor (5) was prepared in the same manner as for photoreceptor 1, except that CTL binder was replaced with simple polycarbonate instead of examplified compound (1)-4 unit repeated polymer.

Preparation of comparative photoreceptor 1

A comparative photoreceptor 1 was prepared in the same manner as for photoreceptor 1, except that a bisphenol A polycarbonate (Panlite K-1300, produced by Teijin Chemicals Ltd.) was used as a CTL binder.

The sensitizing solution was found unstable, poor in retention stability and easily gelable during preparation of the photoreceptor.

Preparation of comparative photoreceptor 2

A comparative photoreceptor 2 was prepared in the same manner as for photoreceptor 1, except that a bisphenol Z polycarbonate (produced by Mitsubishi Gas Chemical Company, Inc.) was used as a CTL binder.

Preparation of developer

(i) Preparation of toner

72 parts by weight of styrene, 10 parts by weight of methyl methacrylate, 14 parts by weight of butyl acrylate, 4 parts by weight of monoacryloyloxyethyl succinate and 0.5 part by weight of zinc oxide were treated to yield a metal-crosslinked styrene-acrylic copolymer resin having a double peak molecular weight distribution, a weight average molecular weight of 170000 and a number average molecular weight of 9000.

Resin obtained above 100 parts by weight

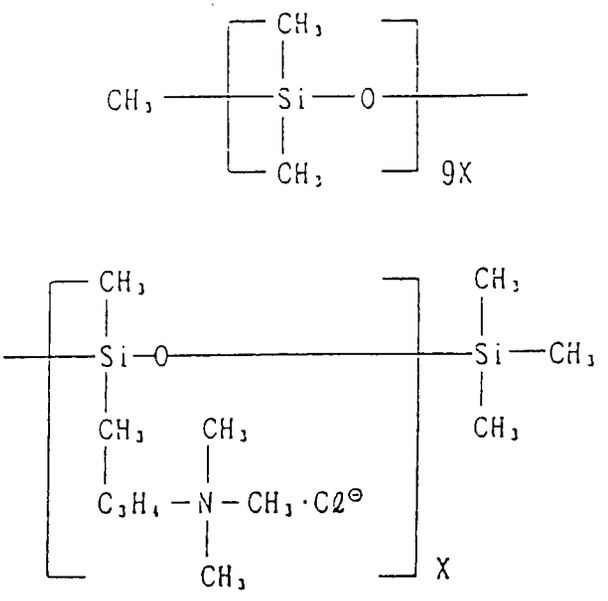
Carbon black Mogal L (produced by Cabot) 10 parts by weight

These substances were mixed, kneaded in a molten state and cooled, after which they were coarsely pulverized and then finely pulverized and classified to yield a toner having an average grain size of 10 μm.

(ii) Preparation of inorganic grains

A polysiloxane having an ammonium salt functional group represented by the following formula was dissolved in xylene to yield a treating solution.

Polysiloxane



X represents an integer.

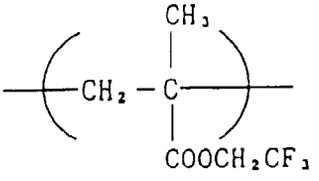
Next, fine grains of silica Aerosil 200 (produced by Nihon Aerosil Co., Ltd.) were placed in a mixer and sprayed with the polysiloxane in a ratio such that the ratio of the polysiloxane was 5 wt%, after which they were transferred to a flask, followed by removing the solvent xylene while stirring at 200°C for 5 hours to yield inorganic fine grains surface treated with the polysiloxane having an ammonium salt functional group.

The inorganic fine grains had a primary grain size of 12 mμ and a specific area of 115 m^2/g as determined by the BET method.

(iii) Preparation of carrier

Using a fluidized bed system, the surface of ferrite grains F-150 (produced by Nippon Teppun Kogyo) was coated with a fluorine resin with the following structure to a film thickness of about 1.5 μm to yield a resin-coated carrier, which had a grain size of 80 μm.

Fluorine resin



First, 0.5 part by weight of the inorganic grains was added to 100 parts by weight of the toner, followed by mixing using a Henshel mixer to adhere the inorganic grains onto the toner grain surface, followed by mixing with the carrier using a V mixer to yield a developer having a toner concentration of 5 wt%.

The inventive photoreceptors 1 through 4 and comparative photoreceptors 1 and 2 were loaded on a version of U-BIX 5000 (produced by Konica Corporation), and the two-component developer was filled in the developing device of the copying machine, and the tests of Table 2 were conducted under the mechanical conditions shown in Table 1. Each test was repeated in 100000 cycles, and the surface potential of the photoreceptor was measured before and after actual imaging.

The black paper potential Vb in Table 2 is the surface potential of the photoreceptor to an original with a reflective density of 1.3. The white paper potential V_W is the surface potential of the photoreceptor to an original with a reflex density of 0. The residual potential V_R is the surface potential of the photoreceptor after discharging. All these values were measured using a voltameter probe placed at the developing device before and after actual imaging.

Film wear due to friction on the photoreceptor surface was determined by measuring the film thickness of the photoreceptor after 100000 copies were taken and compared with the initial value.

As for image quality, the image sample was sequentially checked by counting the copies with visible streaks or cleaning failures associated with flaws in the direction of the drum periphery.

Additionally, the above tests were carried out using photoreceptor 1, setting the peripheral speed of the photoreceptor drum at 616 mm/sec, the peripheral speed of the sleeve at 1078 mm/sec (peripheral speed ratio K = 1.75) and the magnetic flux density on the sleeve at 1050 gauss. (test No. 11)

The results of measurements are given in Table 2. From Table 2, it is evident that the test samples according to the invention show little abrasive wear in the photoreceptor and little flaws or cleaning failures on the photoreceptor surface, while the comparative photoreceptors showed significant wear and deterioration.

Table 1

Copying speed	50 copies/min for A4 size, landscape position
Photoreceptor drum diameter	100 mmØ
Drum peripheral speed	333 mm/sec
Sleeve diameter	55 mmØ
Sleeve peripheral speed	666 mm/sec
Peripheral speed ratio (sleeve/photoreceptor drum)	2.0
Magnetic flux density of main developing magnetic pole	900 gauss, 1050 gauss, 1300 gauss

Table 2

Photo-receptor	Property	Photoreceptor surface potential (V)						Sleeve surface magnetic flux density (gauss)	Film thick-ness after wear (μm)	Image quality	
		Initial			After 100000 copies					Streaks (moderate tone)	Cleaning failure
	Test number	$-V_b$	$-V_W$	$-V_R$	$-V_b$	$-V_W$	$-V_R$				
Inventive photo-receptor 1	Main test 1	700	45	5	710	80	45	1050	1.2	Not found	Not found
	2	705	40	5	710	90	40	1300	2.5	Appeared after 60000 copies	Not found
Inventive photo-receptor 2	3	700	30	5	710	70	50	1050	1.2	Not found	Not found
	4	700	35	5	710	70	45	1300	2.4	Appeared after 60000 copies	Not found
Inventive photo-receptor 3	5	705	60	10	710	90	50	1050	1.3	Not found	Not found
	6	705	65	5	715	95	50	1300	2.4	Appeared after 60000 copies	Not found
Inventive photo-receptor 4	7	700	45	5	710	75	45	1050	1.5	Not found	Not found
	8	700	40	5	715	75	50	1300	2.5	Appeared after 60000 copies	Not found
Inventive photo-receptor 5	9	705	45	5	710	95	45	1050	2.0	Appeared after 80000 copies	Not found
	10	700	50	5	715	105	45	1300	3.5	Appeared after 50000 copies	Not found
Inventive photo-receptor 6	11*)	700	55	10	715	110	55	1050	2.1	Appeared after 80000 copies	Not found
Compara-tive photo-receptor 1	12	705	45	5	715	190	65	1050	8.2	Appeared after 20000 copies	Appeared after 60000 copies
	13	700	40	5	705	125	55	1050	4.2	Appeared after 40000 copies	Appeared after 80000 copies

*) Drum peripheral linear speed (616 mm/sec)

Table 2

Photo-receptor	Property	Photoreceptor surface potential (V)						Sleeve surface magnetic flux density (gauss)	Film thick-ness after wear (μm)	Image quality	
		Initial			After 100000 copies						
	Test number	$-V_b$	$-V_W$	$-V_R$	$-V_b$	$-V_W$	$-V_R$			Streaks (moderate tone)	Cleaning failure
Inventive photo-receptor 1	14	705	45	5	710	80	40	1050	1.3	Not found	Not found
	15	705	40	5	715	90	40	1300	2.5	Appeared after 60000 copies	Not found
Inventive photo-receptor 3	16	705	60	10	710	90	55	1050	1.3	Not found	Not found
	17	700	65	10	705	100	55	1300	2.3	Appeared after 60000 copies	Not found
Compara-tive photo-receptor 1	18	700	45	5	710	180	65	1050	8.5	Appeared after 20000 copies	Appeared after 60000 copies
Compara-tive photo-receptor 2	19	700	40	5	705	125	55	1050	4.2	Appeared after 40000 copies	Appeared after 80000 copies

Form Table 2, it is evident that the test samples according to the present invention showed little wear deterioration and electrophotographic performance degradation during repeated high speed copying, while the comparative samples showed significant wear deterioration in the photoreceptor.

When the magnetic flux density of the main developing magnetic pole was 900 gauss, developer scattering occurred from the initial stage, the photoreceptor lacking practical applicability (the relevant data are not given in Table 2).

As is evident from the description above, the method of image formation of the present invention is effective in stably obtaining high quality images without being accompanied by photoreceptor wear, imaging failure or electrophotographic performance degradation during repeated image formation at high speed.

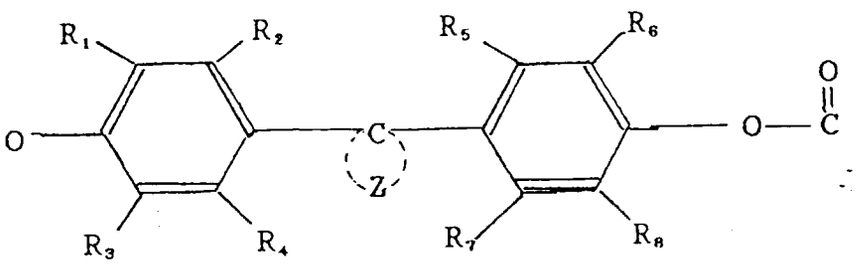
Claims

1. A method of electrophotographic image formation comprising:

rotating an organic photoelectroconductive photoreceptor, and charging and imagewise exposing the rotating photoreceptor to form an electrostatic latent image on the photoreceptor;
rotating a sleeve around a fixed static magnet, which sleeve carries a developing agent for developing the electrostatic latent image, wherein

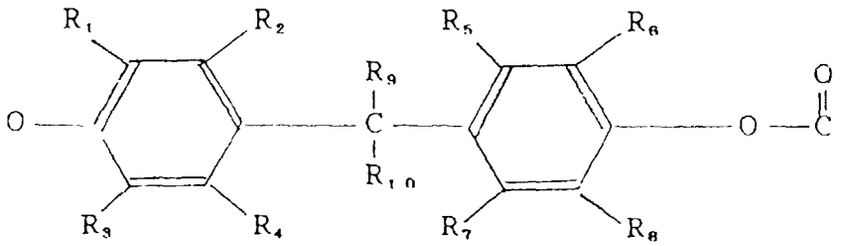
at least the uppermost layer of the photoreceptor comprises a polycarbonate, based on a repeat unit of Formula I or II below;

Formula I,



wherein Z represents a group of atoms necessary to complete a substituted or unsubstituted carbon ring or heterocyclic ring group, R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8 independently represent a hydrogen atom, methyl group, chlorine atom or bromine atom, and at least one of R_1 to R_8 is other than a hydrogen atom;

Formula II



wherein R_1 to R_8 are as defined for Formula I and R_9 and R_{10} each independently represent a hydrogen atom or alkyl group having 1 to 6 carbon atoms, wherein

the magnetic flux density on the sleeve is not less than 950 gauss; and
the peripheral speed of the photoreceptor is not less than 300 mm/sec.

2. The method of claim 1, wherein the repeat unit is represented by Formula I.

3. The method of claims 1 or 2, wherein the magnetic flux density is not more than 1200 gauss, and-the peripheral speed is not more than 600 mm/sec.

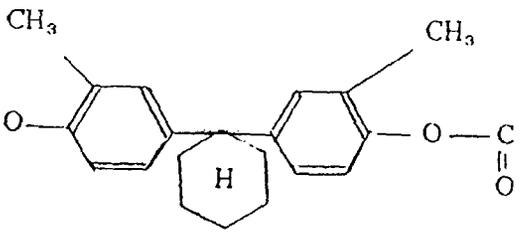
4. The method of any preceding claim, wherein two of R_1 to R_8 comprise methyl groups or chlorine atoms.

5. The method of claim 4, wherein the peripheral speed of the photoreceptor is not less than 350 mm/sec.

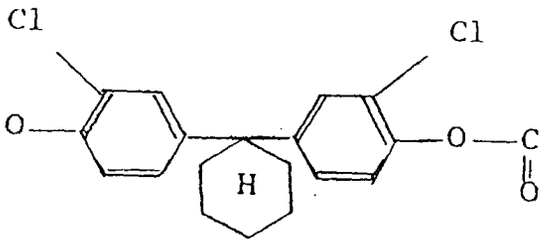
6. The method of any preceding claim, wherein Z completes a cyclohexane group or a cyclopentane group.

7. The method of electrophotographic image formation of claim 1, wherein the photoreceptor is a photoreceptor drum, wherein at least the layer furthermost from the axis of the drum comprises a compound chosen from formulae III, IV, V or VI below;

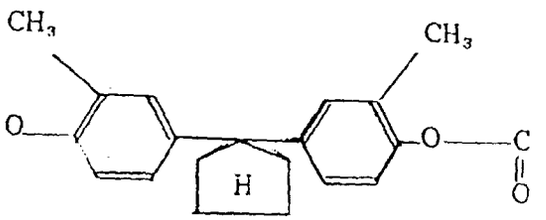
III



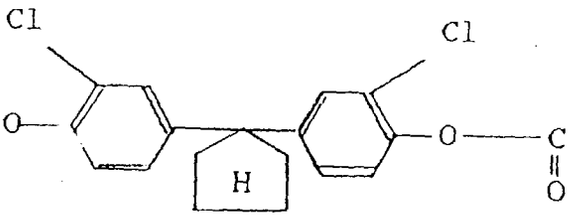
IV



V



VI



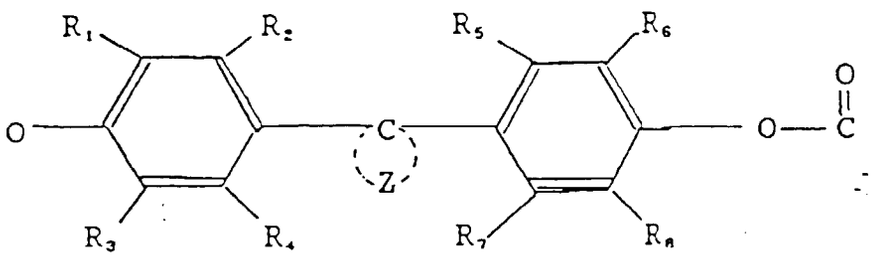
and wherein the magnetic flux density at the sleeve is from 950 to 1200 gauss, and the linear speed of the furthest layer is from 350 to 600 mm/sec.

Patentansprüche

1. Verfahren zur elektrofotografischen Bilderzeugung durch

Drehen eines organischen, fotoelektrisch leitenden Fotorezeptors und Aufladen und bildgerechtes Belichten des sich drehenden Fotorezeptors zur Ausbildung eines latenten elektrostatischen Bildes auf dem Fotorezeptor und
Drehen einer einen Entwickler zum Entwickeln des latenten elektrostatischen Bildes tragenden Hülse um einen eingespannten stationären Magneten, wobei mindestens die oberste Schicht des Fotorezeptors ein Polycarbonat auf der Basis einer wiederkehrenden Einheit der folgenden Formel I oder II umfaßt:

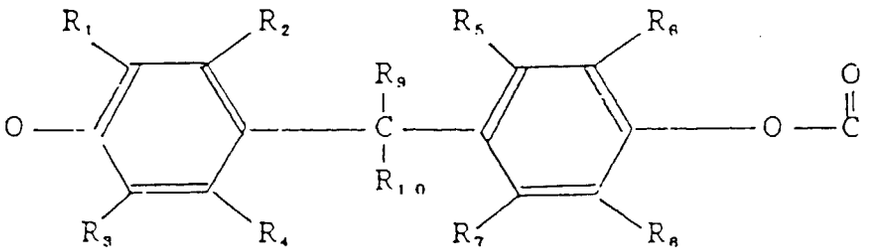
Formel I



worin bedeuten:

Z eine Gruppe von zur Vervollständigung einer gegebenenfalls substituierten Kohlenstoffring- oder heterozyklischen Ringgruppe erforderlichen Atomen und
R_1, R_2, R_3, R_4, R_5, R_6, R_7 und R_8 unabhängig voneinander jeweils ein Wasserstoffatom, eine Methylgruppe, ein Chloratom oder ein Bromatom, wobei mindestens einer der Reste R_1 bis R_8 von einem Wasserstoffatom verschieden ist;

Formel II



worin R_1 bis R_8 die bei Formel I angegebene Definition besitzen und R_9 und R_{10} unabhängig voneinander jeweils für ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen stehen, und wobei die magnetische Flußdichte auf der Hülse nicht weniger als 950 Gauss und die Umfangsgeschwindigkeit des Fotorezeptors nicht weniger als 300 mm/s betragen.

2. Verfahren nach Anspruch 1, wobei die wiederkehrende Einheit der Formel I entspricht.

3. Verfahren nach Anspruch 1 oder 2, wobei die magnetische Flußdichte nicht mehr als 1200 Gauss und die Umfangsgeschwindigkeit nicht mehr als 600 mm/s betragen.

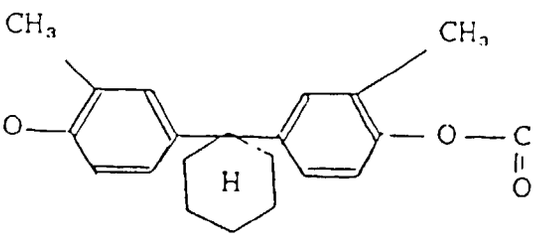
4. Verfahren nach einem der vorhergehenden Ansprüche, wobei zwei der Reste R_1 bis R_8 Methylgruppen oder Chloratome umfassen.

5. Verfahren nach Anspruch 4, wobei die Umfangsgeschwindigkeit des Fotorezeptors nicht weniger als 350 mm/s beträgt.

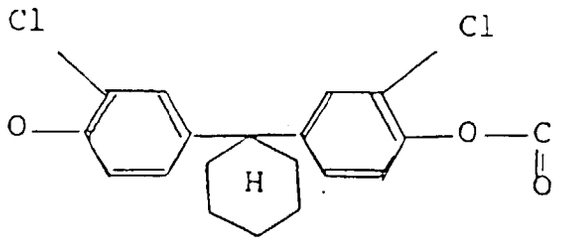
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei Z eine Cyclohexangruppe oder eine Cyclopentangruppe vervollständigt.

7. Verfahren zur elektrofotografischen Bilderzeugung nach Anspruch 1, wobei der Fotorezeptor aus einem trommelförmigen Bildempfangsmaterial besteht, mindestens die von der Trommelachse am weitesten entfernte Schicht eine Verbindung der Formeln III, IV, V oder VI umfaßt:

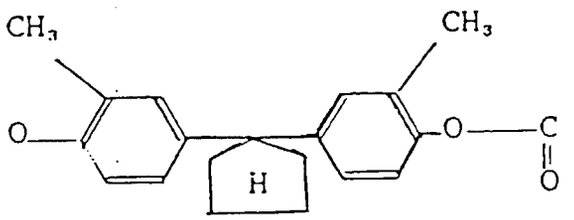
III



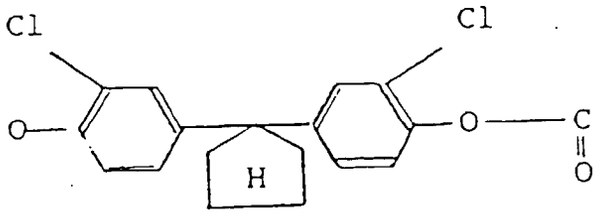
IV



V



VI



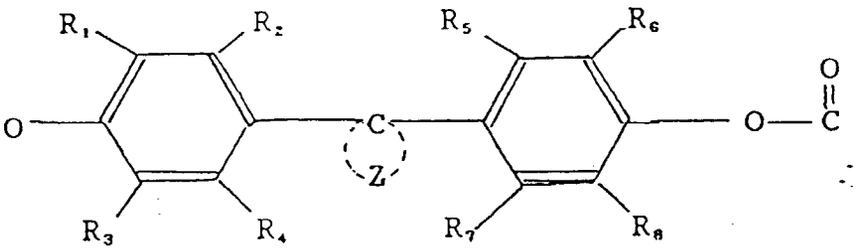
und
die magnetische Flußdichte an der Hülse 950-1200 Gauss und die Lineargeschwindigkeit der am weitesten entfernten Schicht 350-600 mm/s betragen.

Revendications

1. Procédé de formation d'image électrophotographique comprenant les étapes consistant :

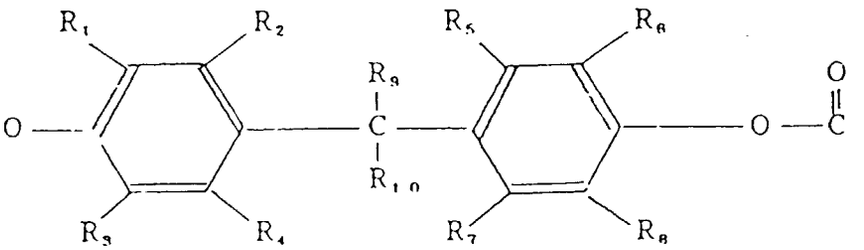
à mettre en rotation un photorécepteur photoélectroconducteur organique et à charger le photorécepteur en rotation et à l'exposer de manière à former une image, afin d'obtenir une image latente électrostatique sur le photorécepteur ;
à faire tourner un cylindre autour d'un aimant statique fixe, lequel cylindre porte un agent développeur destiné à développer l'image latente électrostatique, procédé dans lequel :
au moins la couche supérieure du photorécepteur comprend un polycarbonate, constitué d'unité répétitive de formule I ou II ci-dessous ;

Formule I



où Z représente un groupe d'atomes nécessaires pour compléter un noyau cyclique carboné ou un noyau hétérocyclique substitué ou non substitué, R_1, R_2, R_3, R_4, R_5, R_6, R_7 et R_8 représentent indépendamment un atome d'hydrogène, un groupe méthyle, un atome de chlore ou de brome, et au moins l'un de R_1 à R_8 étant différent d'un atome d'hydrogène ;

Formule II



où R_1 à R_8 sont tels que définis pour la formule I et R_9 et R_{10} représentent chacun indépendamment un atome d'hydrogène ou un groupe alkyle ayant de 1 à 6 atomes de carbone, procédé dans lequel
la densité de flux magnétique sur le cylindre n'est pas inférieure à 950 gauss ; et
la vitesse périphérique du photorécepteur n'est pas inférieure à 300 mm/sec.

2. Procédé selon la revendication 1, dans lequel l'unité répétitive est représentée par la formule I.

3. Procédé selon la revendication 1 ou 2, dans lequel la densité de flux magnétique n'est pas supérieure à 1200 gauss et la vitesse périphérique n'est pas supérieure à 600 mm/sec.

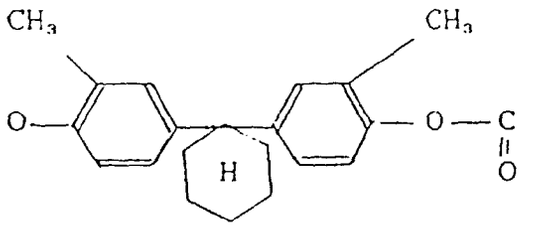
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel deux des radicaux R_1 à R_8 représentent des groupes méthyles ou des atomes de chlore.

5. Procédé selon la revendication 4, dans lequel la vitesse périphérique du photorécepteur n'est pas inférieure à 350 mm/sec.

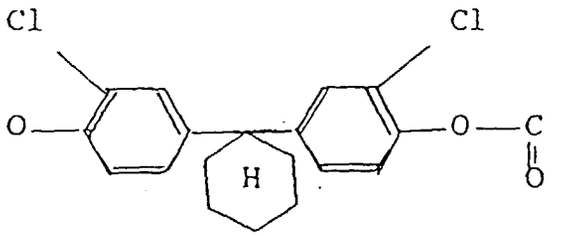
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel Z complète un noyau cyclohexane ou un noyau cyclopentane.

7. Procédé de formation d'image électrophotographique selon la revendication 1, dans lequel le photorécepteur est un tambour photorécepteur, dans lequel au moins la couche la plus éloignée de l'axe du tambour comprend un composé choisi parmi les formules III, IV, V ou VI ci-après ;

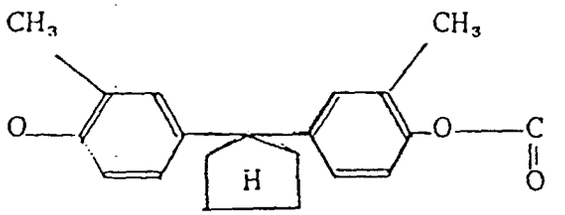
III



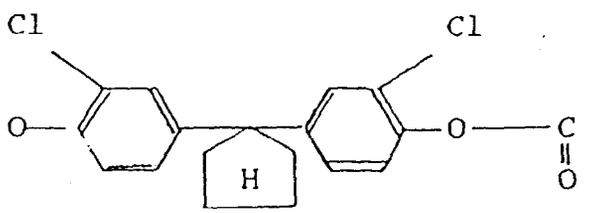
IV



V



VI



et dans lequel la densité de flux magnétique sur le cylindre est de 950 à 1200 gauss, et la vitesse linéaire de la couche la plus éloignée est de 350 à 600 mm/sec.

FIG. 1

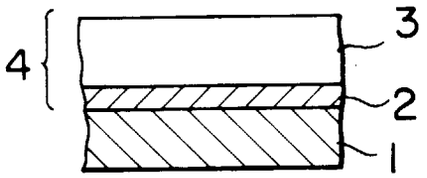


FIG. 2

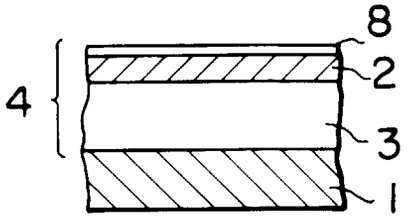


FIG. 3

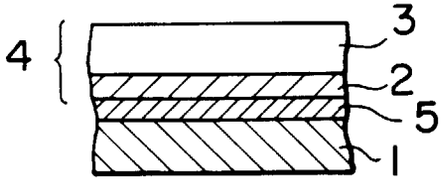


FIG. 4

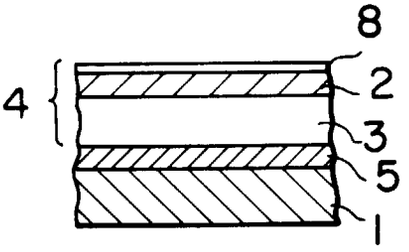


FIG. 5

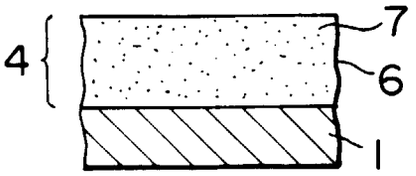


FIG. 6

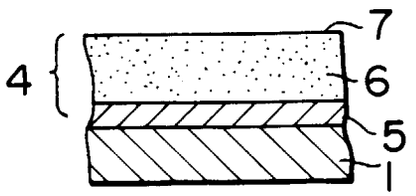
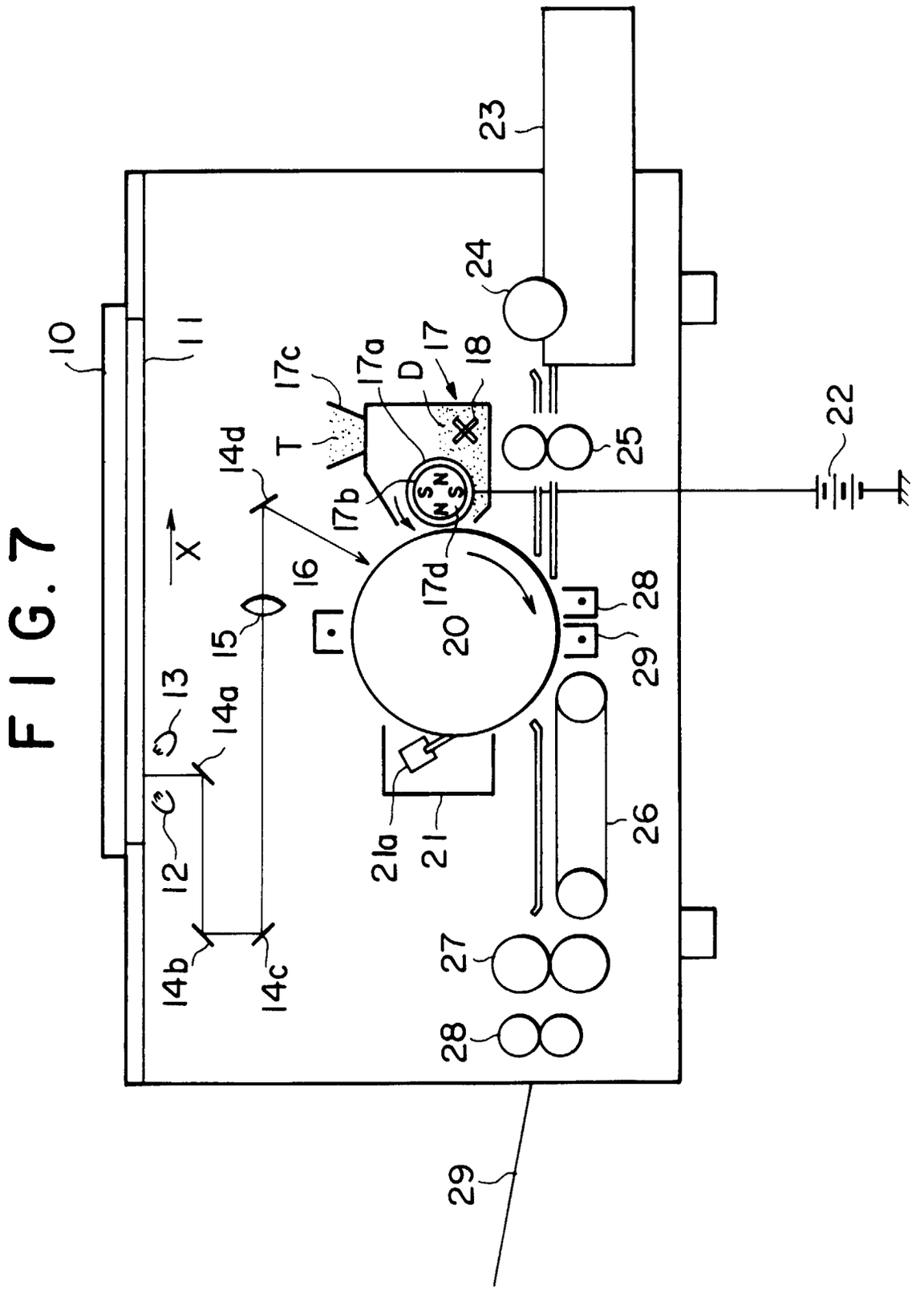


FIG. 7


10
11
12
13
14a
14b
14c
14d
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17a
17b
17c
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