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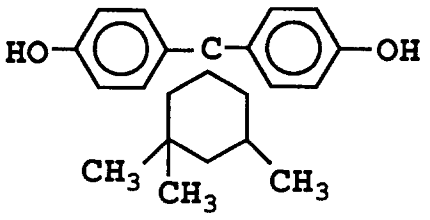
(54) Electrophotographic photosensitive material

(57) An organic electrophotographic photosensitive material highly resistant to stress cracks, solvent cracks and wear, and having markedly improved durability is obtained by incorporating in a binder resin of a charge transport layer (6) of a laminate type photosensitive material a polycarbonate resin prepared using as a starting material a bisphenol compound consisting essentially of a bisphenol compound of the following structural formula (I).



(I)

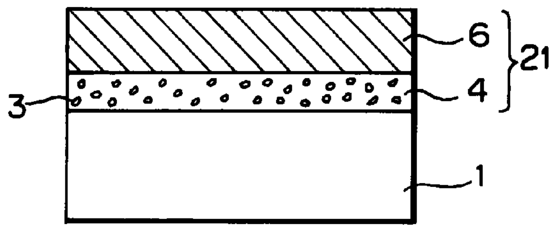


FIG.2

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Description

This invention relates to an electrophotographic photosensitive material, and more specifically, to an organic electrophotographic photosensitive material which contains a specific polycarbonate resin used as a binder resin in a charge transport layer.

Electrophotographic technologies can give high quality images instantaneously, and thus have found wide use in recent years not only in the field of copying machines but in the field of various printers. The core of electrophotographic technologies is electrophotographic photosensitive materials as image forming members. They include conventional inorganic photosensitive materials having a photosensitive layer comprising inorganic photoconductive materials such as selenium, selenium-arsenic alloys, cadmium sulfide, and zinc oxide. Recently, organic photosensitive materials having a photosensitive layer comprising organic photoconductive materials have been developed and have become widespread because of their advantages, such as freedom from pollution, easy film-forming with high productivity, and varieties of materials available. Well known organic photosensitive materials are so-called dispersed single-layer type photosensitive materials having a photosensitive layer comprising a finely divided organic photoconductive material dispersed in a binder resin, and so-called laminate type photosensitive materials having a photosensitive layer comprising a charge generation layer and a charge transport layer laminated together.

Fig. 1 shows the former single-layer type photosensitive material having an electroconductive substrate 1, and a photosesitive layer 20 comprising a finely divided organic photosensitive material dispersed in a binder resin 5.

Fig. 2 shows the latter laminate type photosensitive material comprising an electroconductive substrate 1, and a photosensitive layer 21 provided thereon, the lower one of which is a charge generating layer 4 containing a charge generating substance 3 as the main component, and the upper one of which is a charge transporting layer 6 containing a charge transporting substance.

The latter laminate type photosensitive materials are advantageous in that they are provided with high sensitivity by functionally dividing their photosensitive layer into a charge generation layer for receiving light and generating charge carriers and a charge transport layer for transporting the charge carriers generated, forming these layers from materials optimal for their respective functions, and combining them together as a laminate; that they permit a broad choice of materials and have high safety; and that their productivity is high and their cost relatively low, since the respective layers can be formed as coatings. Thus, they are highly likely to become the mainstream of photosensitive materials, and their commercial use is under way.

Electrophotographic photosensitive materials are required to possess electrical properties, mechanical properties and optical properties adapted to the electrophotographic process applied. The photosensitive materials for repeated use, in particular, are required to be durable to electrical or mechanical force directly applied to their surface layer by corona charge, toner development, transfer to paper or cleaning. That is, they are required to have resistance to deterioration of characteristics such as sensitivity decrease, charge capacity decrease, and residual potential increase due to ozone generated during corona charge; and resistance to wear or scars of the surface of the photosensitive material caused by its abrasion during development, transfer or cleaning.

The surface of organic photosensitive materials is a layer consisting essentially of a resin, and thus the materials are greatly influenced by the characteristics of the resin. The resins that have hitherto been used as satisfying the characteristics required of the surface layer are polycarbonate resins having bisphenol A as the skeleton material. The polycarbonate resins are hereinafter referred to as bisphenol A type polycarbonate resins.

However, bisphenol A type polycarbonate resins do not thoroughly fulfill all of the characteristics required of the resin of photosensitive materials, but they pose the following problems:

(1) They are poorly soluble, and show good solubility in only some halogenated aliphatic hydrocarbons, such as dichloromethane and 1,2-dichloromethane. These halogenated aliphatic hydrocarbons have low boiling points. When coating solutions prepared with these solvents are used to produce photosensitive materials, therefore, the surface of the coating tends to whiten. Process control for the solids in the coating solution is also laborious.

(2) They are soluble in some solvents other than halogenated aliphatic hydrocarbons, such as tetrahydrofuran, dioxane and cyclohexane, or mixtures of these solvents. The resulting solutions are poorly stable over time, as shown by their gelling within a few days, and are not suitable for mass production.

(3) Polycarbonate resins containing only bisphenol A or a bisphenol A derivative as the main skeleton material are apt to undergo solvent cracks.

The problems (1) and (2) about the stability of the solution have been solved by using polycarbonate Z resins having a bulky cyclohexylene group as the structural unit of the polymer. As indicated in the problem (3), however, polycarbonate Z resins and polycarbonate A resins relatively greatly decrease in volume when their solutions are formed into films by casting, and may leave stress behind inside the films. Thus, they have presented the drawback that they are relatively weak to stress cracks. To solve this problem, Japanese Patent Application Laid-Open Patent No. 62040/1986 discloses a method of reducing stress cracks by mixing polycarbonate A resins and polycarbonate Z resins. Also, Japanese Patent

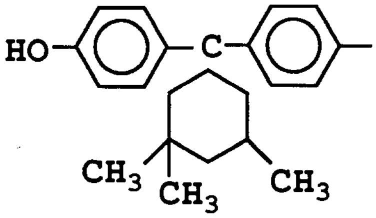
Application Laid-Open No. 62039/1986 discloses a method of decreasing stress cracks by copolymerizing bisphenol A with bisphenol Z. None of these methods, however, have provided sufficient durability to stress cracks.

In recent years, there has been demand for increased sensitivity to be realized in organic photosensitive materials. Because of this demand, low molecular weight compounds such as charge transport substances are frequently used in relatively large amounts. During film formation or during long-term storage, such lower molecular weight components precipitate, causing phase separation.

Furthermore, laminate type organic photosensitive materials now in actual use are inferior to inorganic photosensitive materials, particularly, in terms of durability. One of the factors to determine durability is physical properties. However, the laminate type organic photosensitive materials involve the drawback that they are apt to undergo wear or surface scars due to loads in practical use, such as development with the toner, friction with the paper, and friction with the cleaning member. This drawback has restricted their printing resistance.

This invention has been accomplished in the light of the above drawback. It is aimed at providing an organic photosensitive material highly resistant to stress cracks, solvent cracks and wear, and having markedly improved durability, by incorporating a resin as a binder resin into a charge transport layer, the resin being highly solvent soluble, being highly compatible with a charge transport substance, easily forming a satisfactory film, and having high wear resistance.

This objective can be attained by an electrophotographic photosensitive material having a charge generation layer and a charge transport layer on a conductive substrate, the layers consisting essentially of an organic material, wherein a polycarbonate resin prepared using as a starting material a bisphenol compound consisting essentially of a bisphenol compound of the following structural formula (I) (the polycarbonate resin is referred to hereinbelow as the invented polycarbonate resin)



(I)

is incorporated as a binder resin into the charge transport layer.

This constitution of the invention has been accomplished based on the following findings: We conducted eager studies on the structures of various polycarbonate resins for use as binder resins for the photosensitive layer, and their effects on the characteristics of the charge transport layer. These studies have led us to find that a binder resin containing the above-described invented polycarbonate resin shows excellent solvent solubility and high wear resistance.

The invented polycarbonate resin desirably contains 30 mol % or more of the bisphenol compound of the structural formula (I). If its content is lower, the effect of the invention cannot be exhibited fully. The invented polycarbonate resin has a polystyrene-converted weight average molecular weight (Mw) of 10,000 to 200,000 as measured by gel permeation chromatography (GPC).

The proportion of the invented polycarbonate resin incorporated in the binder resin for the charge transport layer is desirably 80 weight % or more. A lower proportion makes the effect of the invention insufficiently exhibited.

The photosensitive material of the present invention is a laminate type photosensitive material having a photosensitive layer comprising a charge generation layer and a charge transport layer laminated on a conductive substrate. The order of lamination may be such that the charge transport layer is provided on the charge generation layer, or vice versa.

The conductive substrate of the photosensitive material of the invention includes, for example, metallic materials, such as aluminum, stainless steel or nickel; polyester films, phenolic resin pipes, paper tubes or glass tubes, each having on the surface a conductive layer of aluminum, copper, palladium, tin oxide or indium oxide; and plastics containing conductive powder, such as carbon powder, metal powder or metallic oxide powder in dispersed state.

On the conductive substrate, there may be provided an undercoat layer having a barrier function or an adhesive function, if it is necessary. The materials for forming the undercoat layer are, for example, resins such as polyvinyl butyral, polyvinyl alcohol, casein, polyamide, cellulose, gelatin, polyurethane or polyester, and metallic oxides such as aluminum oxide. The thickness of the undercoat layer is preferably 0.1 to 10 μm.

Charge generating substances for use in the charge generation layer are organic pigments such as phthalocyanine pigments, azo pigments, quinacridone pigments, indigo pigments, perylene pigments, polycyclic quinone pigments, anthanthrone pigments, and benzimidazole pigments. When in use, their fine particles are bound with a binder resin such as polycarbonate resin, polyvinyl acetate, polyacrylic ester, polymethacrylic ester, polyvinyl chloride copolymer, polyester, polyvinyl acetoacetal, polyvinyl propional, polyvinyl butyral, phenoxy resin, epoxy resin, urethane resin, cellulose ester, or cellulose ether. The proportion of the charge generating substance is preferably in the range of 30 to

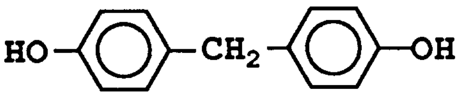
500 parts by weight relative to 100 parts by weight of the binder resin. The thickness of the charge generation layer is desirably 0.1 to 1 μm.

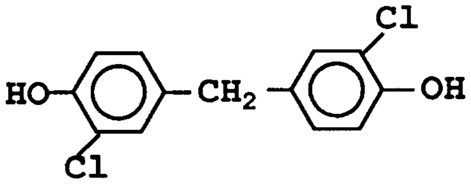
The charge transport layer is formed by converting an enamine compound, a styryl compound, a hydrazone compound, a butadiene compound, an amine compound or the like as the charge transporting substance into a solution together with the binder resin containing the invented polycarbonate resin, and applying the resulting coating solution. The thickness of the charge transport layer is usually 10 to 40 μm. To the charge transport layer may be added a leveling agent and a plasticizer for the purpose of improving the film-forming properties and coating properties. Antioxidants and ultraviolet absorbers may also be added to improve ozone resistance, NO_x resistance, and ultraviolet light resistance.

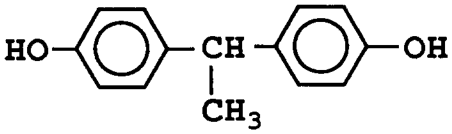
The resin to be used along with the invented polycarbonate resin for the binder resin of the charge transport layer includes, for example, polycarbonate resin other than the invented polycarbonate resin, polyvinyl acetate, polyacrylic ester, polymethacrylic ester, polyester, polyvinyl acetoacetal, polyvinyl propional, polyvinyl butyral, phenoxy resin, epoxy resin, urethane resin, cellulose ester, and cellulose ether.

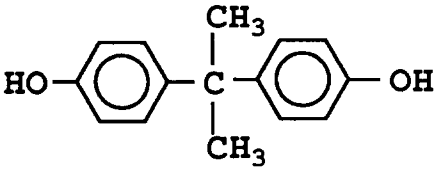
The invented polycarbonate resin can be synthesized easily by mixing the bisphenol compound of the aforementioned structural formula (I) with other bisphenol compound in predetermined proportions, and performing their condensation by a customary method using phosgene.

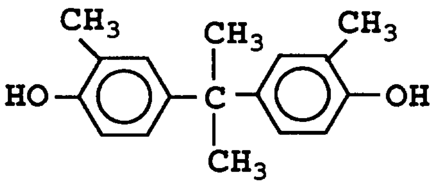
The bisphenol compound other than that of the structural formula (I) includes, for example, compounds of the following structural formulae:

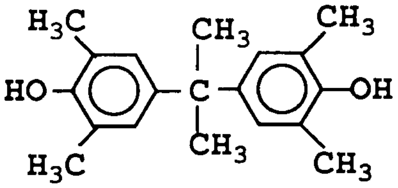


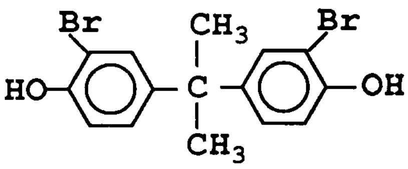


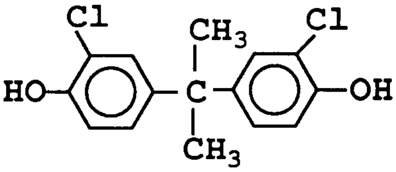


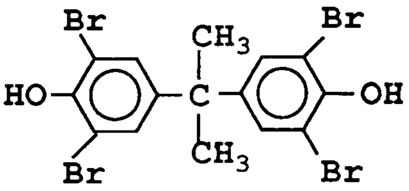


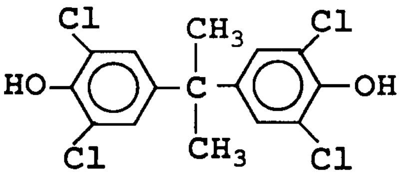


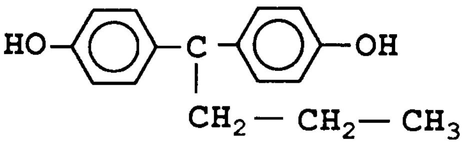


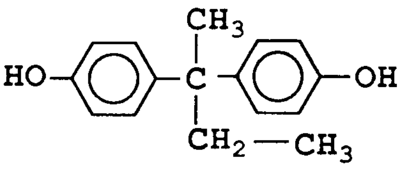


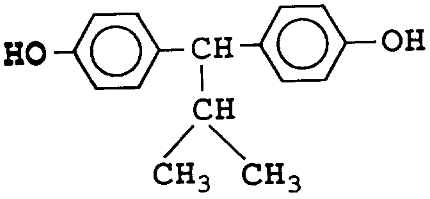








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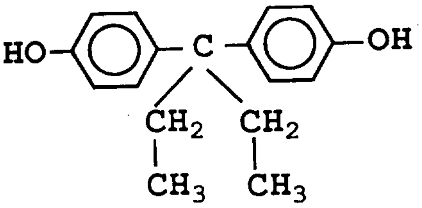
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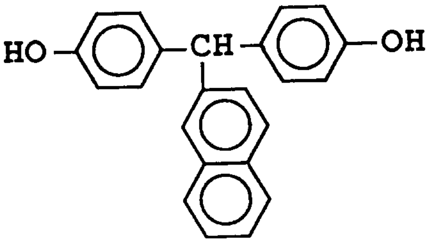
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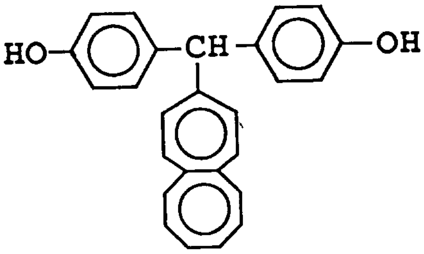
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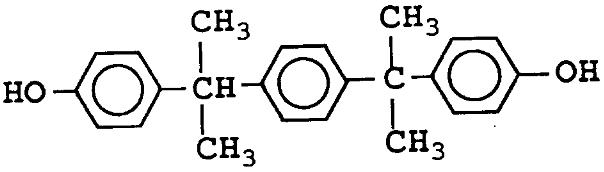
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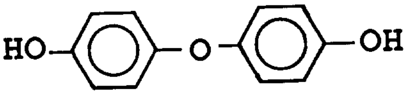
CH3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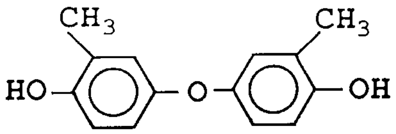
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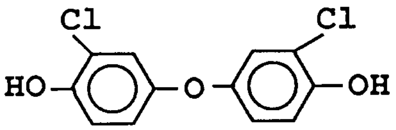
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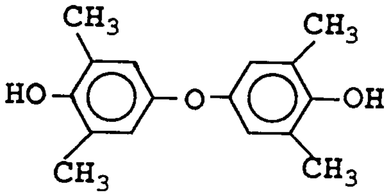
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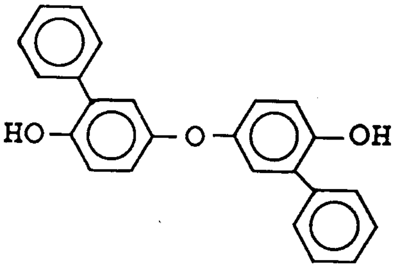
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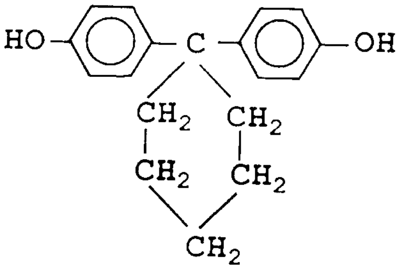
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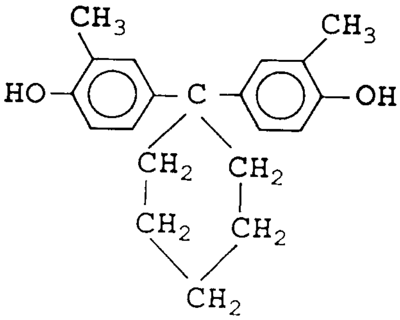
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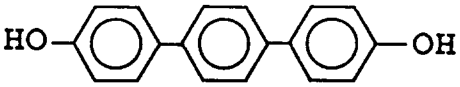

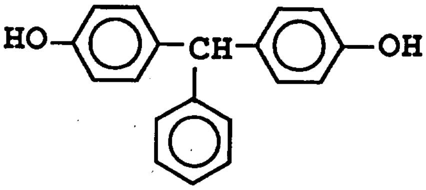

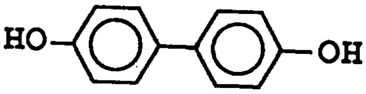

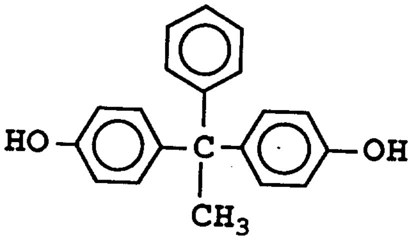

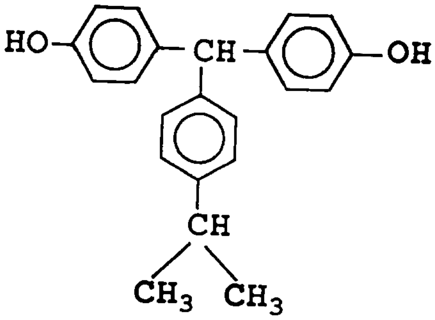

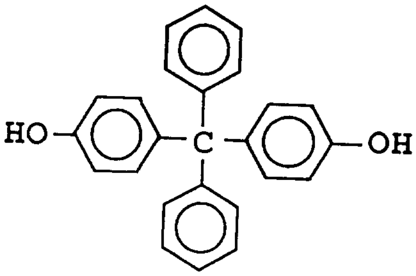

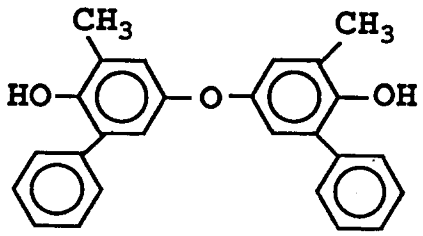

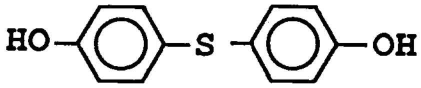

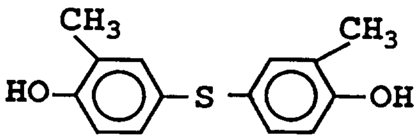

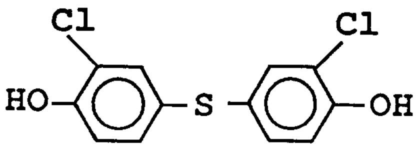

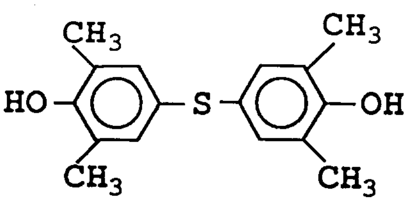
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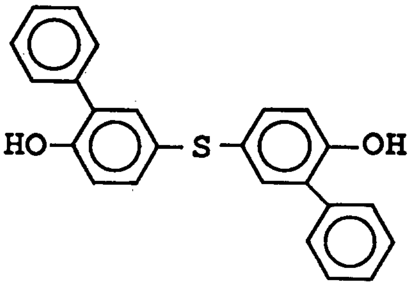
S
OH
CH3
CH3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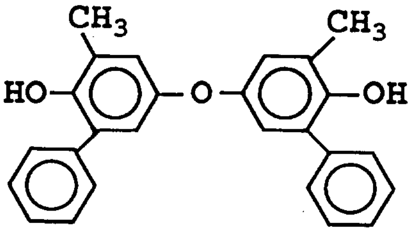
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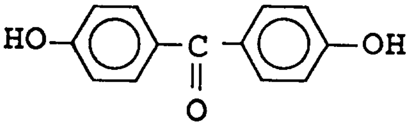
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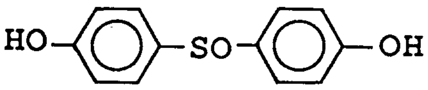
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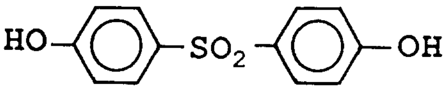
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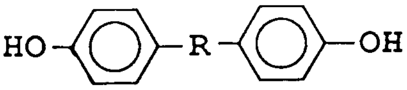
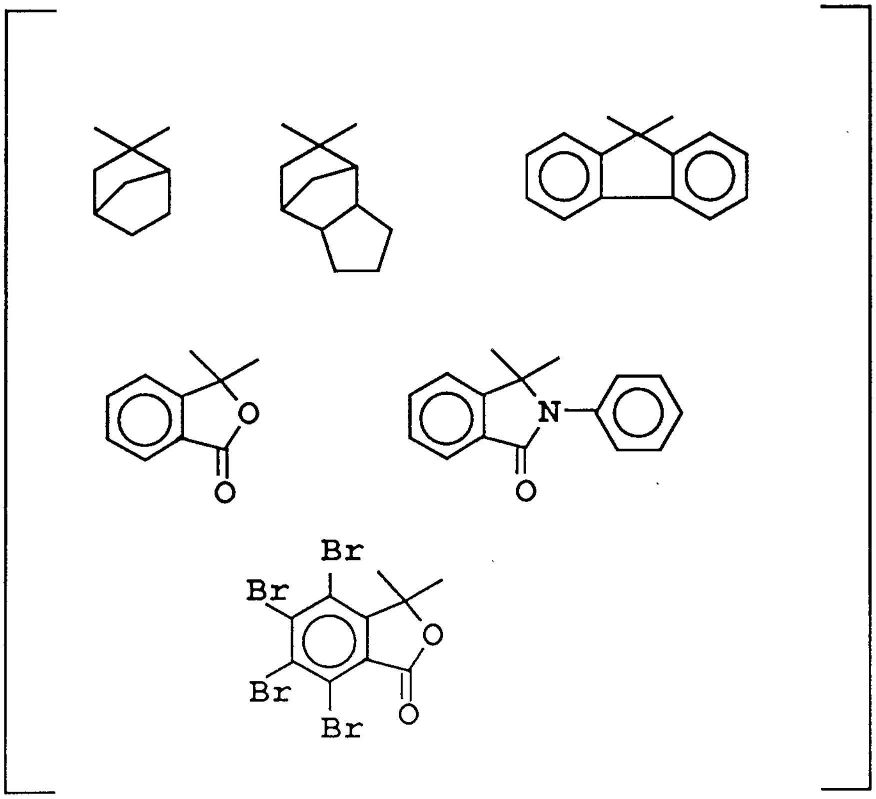
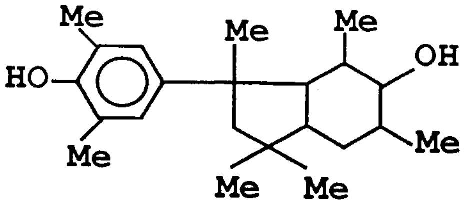
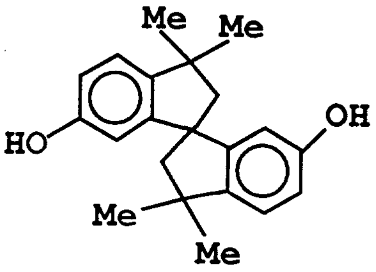

HO
R
OH

where R represents any one of the following formulae







The above and other objects, effects, features and advantages of the present invention will become more apparent from the following description of embodiments thereof.

Fig. 1 is schematic cross-sectional view of a conventional single-layer type photosensitive material.
Fig. 2 is schematic cross-sectional view of a laminate type photosensitive material according to the present invention.

The embodiments of the present invention will be described below.

First, synthesis examples of the invented polycarbonate resin will be offered.

[Synthesis Example 1]

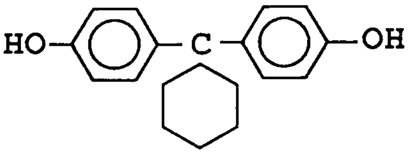
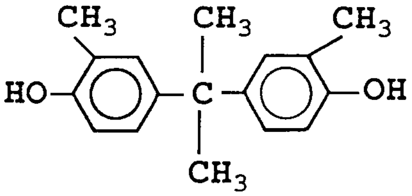
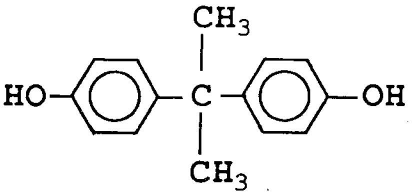
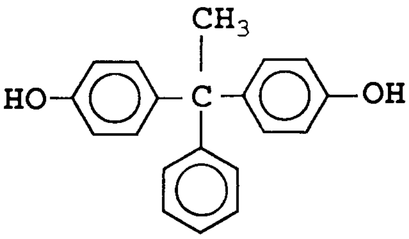
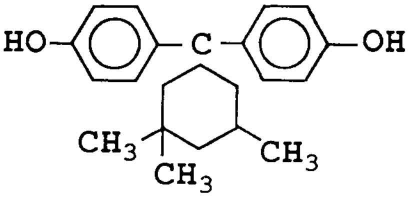
A 3-liter reactor was charged with 0.2 mol of a bisphenol compound of the structural formula (I), 0.1 mol of 2,2-bis(4-hydroxyphenyl)propane, 500 ml of a 5% aqueous solution of NaOH, and 400 ml of methylene chloride. With the charge stirred vigorously, $COCl_2$ was blown therein for 20 minutes at a rate of 500 ml/min. The reaction temperature was held at 15°C. Further, 40 ml of sodium hydroxide at a concentration of 13.7%, 0.2 g of trimethylbenzylammonium chloride, and 0.3 ml of triethylamine were added. With the temperature kept at 23°C, the mixture was stirred for 1 hour to perform a polycondensation reaction. After completion of the reaction, the product was diluted with 400 ml of methylene chloride, and washed with 1 liter of water, 0.5 liter of 0.01N hydrochloric acid, and 1 liter of water in this order. The resulting organic acid was poured into 5 liters of methanol to precipitate a white polymer. After filtration, the filter cake was dried for 12 hours at 100°C to obtain about 100 g of a copolymerized polycarbonate resin. This resin had a molecular weight (Mw), as determined by GPC, of 25,000.

[Synthesis Examples 2 - 6]

Copolymerized polycarbonate resins each weighing about 100 g were obtained in the same manner as in Synthesis Example 1 except that bisphenol compounds of the structural formulae shown in Table 2 were used in place of the 2,2-

bis(4-hydroxyphenyl)propane. The molecular weights (Mw) by GPC of the resulting resins were as shown in Table 2.

Table 2

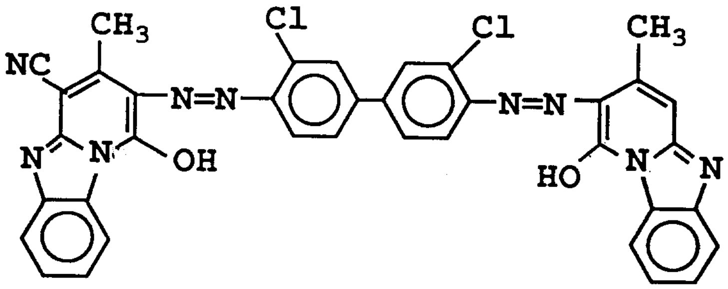
Syn. Ex.	Bisphenol compound	Molecular weight (Mw)
2		35,000
3		20,000
4		30,000
5		17,000
6		50,000

[Synthesis Example 7]

Copolymerized polycarbonate resin was obtained in the same manner as in Synthesis Example 1 using 0.045 mol of the bisphenol compounds of the structural formula (1) and 0.255 mol of the 2,2-bis(4-hydroxyphenyl)propane. The molecular weights (Mw) by GPC of the resulting resins was 60,000.

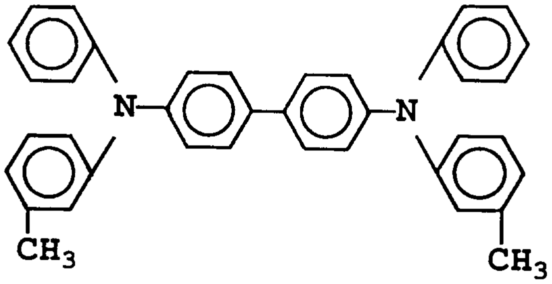
[Example 1]

2.1 Parts by weight of a bisazo compound of the following structural formula

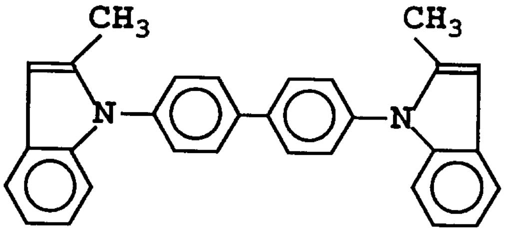


was dispersed by a sand mill together with 1.0 part by weight of a polyvinyl acetal (ESLEX KS-1, a product of Sekisui Chemical Co., Ltd.), 16 parts by weight of methyl ethyl ketone, and 9 parts by weight of cyclohexanone, followed by further adding 75 parts by weight of methyl ethyl ketone, to prepare a coating fluid. The coating fluid was coated onto the surface of an aluminum cylinder (outside diameter 60 mm, length 348 mm, and thickness 1 mm) provided beforehand with a 0.5 µm thick film of a soluble polyamide resin (DIAMIDE T-171, a product of Daicel Hurus) to form a charge generation layer with a dry-basis thickness of 0.2 µm.

Separately, 10 parts by weight of the polycarbonate resin prepared in Synthesis Example 1, 7 parts by weight of a charge transporting substance of the following structural formula (A), and 3 parts by weight of a charge transporting substance of the following structural formula (B)



---------------- (A)



---------------- (B)

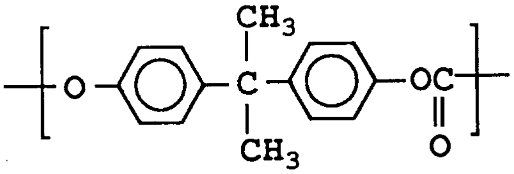
were dissolved in 80 parts by weight of tetrahydrofuran to obtain a coating solution for constituting a charge transport layer. This coating solution was coated onto the above-described charge generation layer to form a charge transport layer with a dry-basis thickness of 30 µm. Thus, a photosensitive material of Example 1 with the structure shown in Fig. 2 was produced.

[Examples 2 to 7]

Photosensitive materials of Examples 2 to 7 with the stucture shown in Fig. 2 were produced in the same manner as described above except that the polycarbonate resin used for the charge transport layer was replaced by each of the resins prepared in Synthesis Examples 2 to 7.

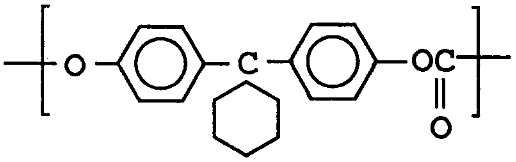
[Comparative Example 1]

A photosensitive material with the stucture shown in Fig. 2 was produced in the same way as in Example 1 except that the polycarbonate resin used for the charge transport layer was replaced by a resin of the following structural formula which had a molecular weight (Mw) of 40,000.



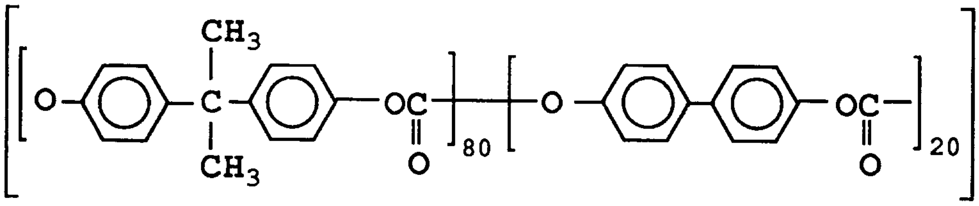
[Comparative Example 2]

A photosensitive material with the stucture shown in Fig. 2 was produced in the same way as in Example 1 except that the polycarbonate resin used for the charge transport layer was replaced by a resin of the following structural formula which had a molecular weight (Mw) of 40,000.



[Comparative Example 3]

A photosensitive material with the stucture shown in Fig. 2 was produced in the same way as in Example 1 except that the polycarbonate resin used for the charge transport layer was replaced by a resin of the following structural formula which had a molecular weight (Mw) of 40,000.



The coating solutions used for the formation of the charge transport layer in Examples 1 to 7 and Comparative Examples 1 to 3 were allowed to stand at room temperature, and observed for stability. Moreover, each of the coating solutions was coated onto a glass plate, and a fingerprint was applied. After the coating was allowed to stand for 1 day in an atmosphere at a temperature of 60°C and a relative humidity of 90%, it was observed for the occurrence of cracks.

The results are shown in Table 3.

Table 3

	Stability of coating solution	Cracking
Ex.1	Good	None
Ex.2	Good	None
Ex.3	Good	None
Ex.4	Good	None
Ex.5	Good	None
Ex.6	Good	None
Ex.7	Good	None
Comp.Ex.1	Whitened after 1 day	Marked cracking
Comp.Ex.2	Good	Moderate cracking
Comp.Ex.3	Whitened after 1 day	Marked cracking

As shown in Table 3, the coating solutions for the charge transport layers of Examples 1 to 7 were well stable, and their coatings developed no cracks. The coating solutions of Comparative Examples 1 and 3 had poor stability, developing whitening when left to stand for 1 day. Their coatings also showed large cracks. The coating solution of Comparative Example 2 had satisfactory stability, but cracks occurred in its coating. Thus, the invented polycarbonate resin is clearly effective.

Next, each of the photosensitive materials of Examples 1 to 7 and Comparative Examples 1 to 3 was mounted on a commercially available copying machine (PP-3380, a product of Matsushita Electric Industrial Co., Ltd.). After 100,000 copies were made using a A4-size paper, the photosensitive materials were examined for fluctuations in the electrical characteristics, decreases in film thickness, and changes in image quality. The results are shown in Table 4-1 and 4-2. The film thickness can be regarded as the thickness of the charge transport layer, since the thickness of the charge generation layer is 0.2 μm. Thus, the decrease in film thickness may be considered the decrease in the thickness of the charge transport layer.

Table 4-1

	Characteristics at initial stage			
	Light paper potential (V)	Black paper potential (V)	Film thickness (μm)	Image quality
Ex.1	-700	-65	30	Good
Ex.2	-700	-55	30	Good
Ex.3	-700	-50	30	Good
Ex.4	-700	-60	30	Good
Ex.5	-700	-60	30	Good
Ex.6	-700	-65	30	Good
Ex.7	-700	-60	30	Good
Comp.Ex.1	-700	-70	30	Good
Comp.Ex.2	-700	-50	30	Good
Comp.Ex.3	-700	-50	30	Good

Table 4-2

	Characteristics after 100,000 copies			
	Light paper potential (V)	Black paper potential (V)	Film thickness (µm)	Image quality
Ex.1	-680	-70	28	Good
Ex.2	-670	-60	26	Good
Ex.3	-650	-55	27	Good
Ex.4	-680	-70	26	Good
Ex.5	-670	-68	28	Good
Ex.6	-660	-70	27	Good
Ex.7	-680	-70	28	Good
Comp.Ex.1	-580	-80	23	White blank
Comp.Ex.2	-600	-60	24	Many black spots
Comp.Ex.3	-650	-58	25	Many black spots

As shown in Table 4-1 and 4-2, the photosensitive materials of Examples 1 to 7 were stable in electrical characteristics and film thickness, and gave stably good image quality at the initial stage and after making 100,000 copies. The photosensitive materials of Comparative Examples 1 to 3, by contrast, underwent great fluctuations in electrical characteristics, marked decreases in film thickness, white blank and black spots occurrence in image owing to the preparation of 100,000 copies. Thus, it is evident that the incorporation of the invented polycarbonate resin into the charge transport layer markedly improved the durability of the photosensitive material.

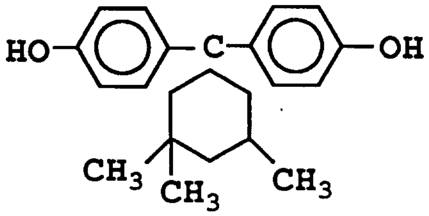
According to this invention, in an electrophotographic photosensitive material having a charge generation layer and a charge transport layer on a conductive substrate, the layers consisting essentially of an organic material, a polycarbonate resin prepared using as a starting material a bisphenol compound consisting essentially of a bisphenol compound of the aforementioned structural formula (I) is incorporated as a binder resin into the charge transport layer. The invented polycarbonate resin with such a feature is highly solvent soluble, is highly compatible with the charge transport substance, easily forms a satisfactory film, and has high wear resistance. By incorporating such a resin in the binder resin of the charge transport layer, it becomes possible to obtain an organic electrophotographic photosensitive material highly resistant to stress cracks, solvent cracks and wear, and having markedly improved durability.

The present invention has been described in detail with respect to preferred embodiments, and it will now be clear that changes and modifications may be made without departing from the invention in its broader aspects, and it is our intention, therefore, in the appended claims to cover all such changes and modifications as falling within the true spirit of the invention.

Claims

1. An electrophotographic photosensitive material characterized by having a charge generation layer and a charge transport layer on a conductive substrate, the layers consisting essentially of an organic material, wherein a copolymerized polycarbonate resin prepared using as a starting material a bisphenol compound consisting essentially

of a bisphenol compound of the following structural formula (I)



(I)

is incorporated as a binder resin into the charge transport layer.

2. An electrophotographic photosensitive material as claimed in claim 1, characterized in that the polycarbonate resin is incorporated in a proportion of 80 wt.% or more based on the binder resin of the charge transport layer.

3. An electrophotographic photosensitive material as claimed in claim 1, characterized in that the content of the bisphenol compound of the structural formula (I) contained in the bisphenol compound, the constituent material for the polycarbonate resin, is 10 mol% or more.

4. An electrophotographic photosensitive material as claimed in claim 1, characterized in that the polycarbonate resin has a polystyrene-converted weight average molecular weight of 10,000 to 200,000.

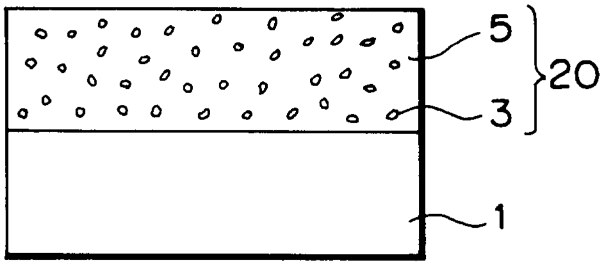


FIG.1
(PRIOR ART)

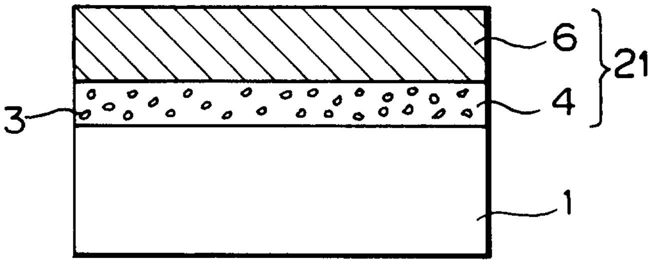


FIG.2

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 2591

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO-A-93 24861 (AGFA) * page 14; examples B5,B6 * ---	1-4	G03G5/05 G03G5/147
A	US-A-5 139 908 (AKASAKI ET AL.) * column 12; examples I-13 * * column 15; examples I-24 * ---	1-4	
A	EP-A-0 356 246 (KONICA) * page 11, line 44 - page 12, line 2 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 December 1995	Vogt, C

CATEGORY OF CITED DOCUMENTS

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