



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 450 599 A1**

12

EUROPEAN PATENT APPLICATION

21 Application number: **91105260.3**

51 Int. Cl.⁵: **G03G 5/14**

22 Date of filing: **03.04.91**

30 Priority: **04.04.90 JP 88294/90**

43 Date of publication of application:
09.10.91 Bulletin 91/41

84 Designated Contracting States:
DE GB IT

71 Applicant: **NEC CORPORATION**
7-1, Shiba 5-chome Minato-ku
Tokyo 108-01(JP)

72 Inventor: **Gotoh, Tomohisa**
c/o Nec Corporation, 7-1, Shiba 5-chome
Minato-ku, Tokyo(JP)

74 Representative: **Pätzold, Herbert, Dr.**
Steubstrasse 10
W-8032 Gräfelfing-München(DE)

54 **An electrophotographic photosensitive material.**

57 An electrophotographic photosensitive material layer of which an undercoat layer contains a partial N-methoxymethylated polyamide resin. The electrophotographic photosensitive material layer is excellent in an electric chargeability, has a high sensitivity, is very superior in industrial fields, and is useful as an electrophotographic photosensitive material for an optical printer such as a laser beam printer, etc.

EP 0 450 599 A1

Field of the invention

The present invention relates to an electrophotographic photosensitive material, and more particularly to an electrophotographic photosensitive material which is improved in electric chargeability and sensitivity by using a specific compound as an undercoat layer of an electrophotographic photosensitive material layer.

Description of the Prior Art

As for a photoconductive material of a photosensitive material used in an electrophotographic system in the past, an inorganic material such as selenium (Se), cadmium sulfide (CdS), zinc oxide (ZnO), amorphous silicon (a-Si) or the like is used. While those inorganic photo sensitive materials have many advantages, simultaneously they have also various disadvantages, for example, they are harmful, expensive and so on. Therefore many organic photosensitive materials using organic substances without such disadvantages have recently been proposed and put to practical use.

As for structures of those photosensitive materials, there are a multilayer structure having a function separation type photosensitive material which includes, as separate layers, a material generating electric charge carriers (hereinafter called a charge generation material) and a material which receives the generated electric charge carriers and transports them (hereinafter called a charge transport material); and a single layer structure having a single layer type photosensitive material which executes generation of electric charge carriers and transportation of electric charge by means of the same material. The multilayer structures are adopted more than the single layer structures because the formers have the larger range of selection of materials and have higher sensitivity than the latter.

Further, there is provided an undercoat layer between an electrophotographic photosensitive material layer and a conductive substrate so that the retention factor of the charged potential of the electrophotographic photosensitive material layer can be increased.

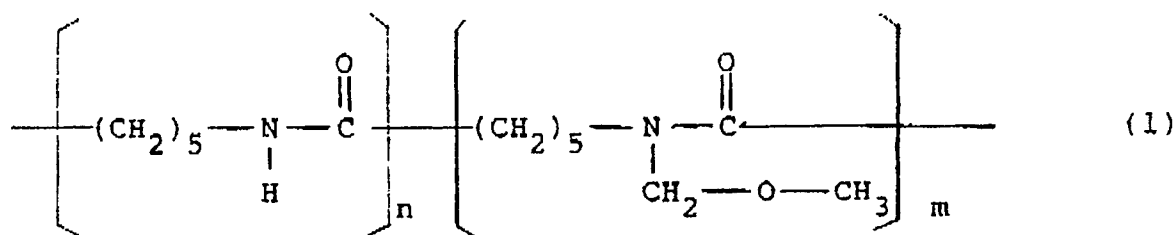
In the above-mentioned undercoat layer, though the retention factor of the surface potential is improved by increasing its film thickness, the sensitivity of the electrophotographic photosensitive material layer deteriorates and the residual potential rises, because carrier injection from the photosensitive material layer to the conductive substrate deteriorates upon exposure.

SUMMARY OF THE INVENTION

The present invention is made in consideration of the foregoing conventional circumstances. The object of the present invention is to provide an electrophotographic photosensitive material using an undercoating material which is excellent in the retention factor of the surface potential of the electrophotographic photosensitive material layer and in which the carrier injection is properly caused upon exposure.

It has been found that it is possible to obtain an undercoat material which is soluble in a lower alcohol and shows less reduction of the sensitivity and no rise of the residual potential when the film thickness is increased, by partially N-methoxymethylating the amide bonding of nylon-6.

Thus, the present invention provides an electrophotographic photosensitive material comprising an undercoat layer and an electrophotographic photosensitive material layer which are successively laminated on a surface of a conductive substrate, wherein said undercoat layer contains a high molecular substance which is represented by the general formula (1):



(wherein m/n represents a real number equal to or larger than 0.1 and n is not zero).

A charge generation material, which is contained in the electrophotographic photosensitive material layer, preferably includes, as the effective components, a composition crystal, which contains a total of not more than 50 parts by weight of one or more kinds from among metal-free aza-phthalocyanine porphyrin derivatives, metallo-aza-phthalocyanine porphyrin derivatives, metal-free phthalocyanine, metallo-

phthalocyanine, metal-free naphthalocyanine or metallo-naphthalocyanine (wherein metal-free aza-phthalocyanine porphyrin derivatives, metallo-aza-phthalocyanine porphyrin derivatives, metal-free phthalocyanine and metallo-phthalocyanine may have a substitutional group in the benzene nucleus, and metal-free naphthalocyanine and metallo-naphthalocyanine may have a substitutional group in the naphthyl nucleus) and 100 parts by weight of titanyl phthalocyanine, and the above-mentioned composition crystal preferably has in its infrared absorption spectrum characteristically strong absorptions at absorption wavelength of $1490 \pm 2 \text{ cm}^{-1}$, $1415 \pm 2 \text{ cm}^{-1}$, $1332 \pm 2 \text{ cm}^{-1}$, $1119 \pm 2 \text{ cm}^{-1}$, $1072 \pm 2 \text{ cm}^{-1}$, $1060 \pm 2 \text{ cm}^{-1}$, $961 \pm 2 \text{ cm}^{-1}$, $893 \pm 2 \text{ cm}^{-1}$, $780 \pm 2 \text{ cm}^{-1}$, $751 \pm 2 \text{ cm}^{-1}$ and $730 \pm 2 \text{ cm}^{-1}$.

A partial N-methoxymethylated amide resin, which is used for the undercoat layer according to the present invention, can be synthesized by reacting nylon-6 with formaldehyde and methanol. The molecular weight of this resin is preferably 1,000 to 500,000. With the increase of the degree of substitution of methoxymethyl, crystallinity drops, and the melting point and the softening temperature also fall, in the amide resin. Thus, when the degree of substitution of methoxymethyl is about 30 %, the softening temperature becomes about 150 to 160 °C. As for the undercoat material for the electrophotographic photosensitive material, the resin in which the degree of substitution of methoxymethyl is of about 18 % to 60 % is preferred.

The partial N-methoxymethylated amide resin is soluble in aliphatic lower alcohol such as methyl alcohol, ethyl alcohol, N-propyl alcohol, isopropyl alcohol or the like, and aromatic alcohol such as phenol, cresol or the like. It is desirable to dissolve the resin in solvent by stirring for about one hour while heating.

The coating can be applied by the use of a coating method such as dip coating, spray coating, wire bar coating, blade coating, roller coating or the like. It is desired for the thickness of the undercoat layer to be about 0.1 to 2.0 μm .

As for the structure of the photosensitive material according to the present invention, there is a structure in which an electrophotographic photosensitive material layer is functionally separated into a charge generation layer 3 and a charge transport layer 4, as shown in Fig. 1. And, as shown in Fig. 2, there may be also used a structure in which a charge generation material and a charge transport material are dispersed in a electrophotographic photosensitive material layer 5. Each of such electrophotographic photosensitive material layers can be formed on a conductive substrate 1 through an undercoat layer 2.

As for the conductive substrate which is used in the present invention, there are used a plastic film provided with a metallic plate, a metallic drum or a metallic foil, which is respectively made of aluminum, nickel, chromium or the like; a plastic film provided with a thin layer made of tin oxide, indium oxide, chromium or the like; a sheet of paper or a plastic film to which a conductive material is coated or impregnated; or the like.

As for the charge generation material, an inorganic material such as Se, CdS or the like which is a well-known photoconductive material, a phthalocyanine containing a metal atom such as Cu, Al, In, Ti, Pb, V or the like, or an organic material such as azo-pigment, his-azo pigment cyanine pigment or the like can be used either singularly or in combination thereof. High sensitivity can be obtained, particularly when titanyl phthalocyanine composition crystal, which is shown in European Patent Application No. 90 11 0693.0, is used among them. The European Patent Application was filed on June 5, 1990 and was published on under No. _____.

As for the binder resin which is used upon forming the charge generation layer by coating, the resin can be selected from among various kinds of insulation resins and can also be selected from organic photoconductive polymer such as poly-N-vinyl carbazole, polyvinyl anthracene, polyvinyl pyrene or the like. Preferably, phenol resin, urea resin, melamine resin, epoxy resin, silicon resin, vinyl chloride-vinyl acetate copolymer, butylal resin, xylene resin, urethane resin, acrylic resin, polycarbonate resin, polyacrylate resin, saturated polyester resin, phenoxy-resin or the like may be mentioned.

The ratio of the charge generation material such as a phthalocyanine compound, etc. which is contained in the charge generation layer is 0.05 to 90 weight % of the generation layer and preferably, 30 to 65 %.

Solvents which dissolve those resins are different according to the kinds of the resins. It is desirable to select among the solvents mentioned later which do not dissolve the charge transport layer or the undercoat layer. As for the practical organic solvents, a ketone such as acetone, methyl ethyl ketone, cyclohexane or the like; an amide such as N,N-dimethyl-formamide, N,N-dimethylacetamide or the like; an ether such as tetrahydrofuran, dioxane, ethylene glycol monomethyl ether or the like; an ester such as methyl acetate, ethyl acetate or the like; an aliphatic hydrocarbon halogenide such as chloroform, methylene chloride, dichloroethylene, carbon tetrachloride, trichloroethylene or the like; or an aromatic compound such as benzene, toluene, xylene, monochlorobenzene, dichlorobenzene or the like can be used. Then it is desirable that the film thickness of the charge generation layer may be 0.1 to 0.5 μm so as to ensure the good sensitivity.

The charge transport layer may be formed either by singularly using a charge transport material or by dissolving and dispersing a charge transport material in a binding resin. As for the charge transport material, any known charge transport agent of a hole transport type can be used.

As for the hole transport material, pyrene,

- 5 N-ethylcarbazole,
N-isopropylcarbazole,
N-methyl-N-phenylhydrazino-3-methylidene-9-ethylcarbazole,
N,N-diphenylhydrazino-3-methylidene-9-ethylcarbazole,
N,N-diphenylhydrazino-3-methylidene-10-ethylphenothiazine,
10 N,N-diphenylhydrazino-3-methylidene-10-ethylphenoxazine,
a hydazone such as
P-diethylaminobenzaldehyde-N,N-diphenylhydrazone,
p-diethylaminobenzaldehyde-N-naphthyl-N-phenylhydrazone,
2-methyl-4-dibenzylaminobenzaldehyde-1'-ethyl-1' -benzothiazolyhydrazone,
15 2-methyl-4-dibenzylaminobenzaldehyde-1'-propyl-1' -benzothiazolyhydrazone,
2-methyl-4-dibenzylaminobenzaldehyde-1',1' -diphenylhydrazone,
9-ethylcarbazole-3-carboxaldehyde-1'-methyl-1'-phenylhydrazone,
1-benzyl-1,2,3,4-tetrahydroquinoline-6-carboxaldehyde-1',1'-diphenylhydrazone,
p-diethylbenzaldehyde-3-methylbenzthiazolinone-2-hydrazone
20 or the like;
2, 5-bis(p-diethylaminophenyl)-1,3,4-oxadiazole,
a pyrazoline such as
1-phenyl-3-(p-diethylaminostyryl) -5-(p-diethylaminophenyl) pyrazoline,
1-[quinolyl(2)]-3-(p-diethylaminostyryl)-5-(p-diethylaminophenyl) pyrazoline,
25 1-[pyridyl(2)]-3-(p-diethylaminostyryl)-5-(p-diethylaminophenyl) pyrazoline,
1-[6-methoxy-pyridyl(2)]-3-(p-diethylaminostyryl)-5-(p-diethylaminophenyl) pyrazoline,
1-[pyridyl(3)]-3-(p-diethylaminostyryl)-5-(p-diethylaminostyryl) pyrazoline,
1-[pyridyl(2)]-3-(p-diethylaminostyryl)-4-methyl-5-(p-diethylaminophenyl) pyrazoline,
1-[pyridyl(2)]-3-(α -methyl-p-diethylaminostyryl)-5-(p-diethylaminophenyl) pyrazoline,
30 l-phenyl-3-(p-diethylaminostyryl)-4-methyl-5-(p-diethylaminophenyl) pyrazoline,
1-phenyl-3-(α -benzyl-p-diethylaminostyryl)-5-(p-diethylaminophenyl)-6-pyrazoline,
spiropyrazoline or the like;
an oxazole compound such as
2-(p-diethylaminostyryl)-6-diethylaminobenzoxazole,
35 2-(p-diethylaminophenyl)-4-(p-diethylaminophenyl)-5-(2-chlorophenyl)-oxazole or the like;
a triarylmethane compound such as
bis(4-diethylamino-2-methylphenyl)-phenylmethane or the like;
a polyarylethane such as
1,1-bis(4-N,N-diethylamino-2-methylphenyl) heptane,
40 1,1,2,2-tetrakis(4-N,N-dimethylamino-2-methylphenyl) ethane or the like;
a stilbene compound such as
1,1-diphenyl-p-diphenylaminoethylene or the like;
a triarylamine compound such as
4,4'-3-methylphenylphenylaminobiophenyl or the like;
45 poly-N-vinyl-carbazole,
polyvinyl pyrene,
polyvinyl anthracene,
polyvinyl acridine,
poly-9-vinylphenylanthracene,
50 pyrene-formaldehyde resin,
polysilylene resin such as polymethylphenylsilirene or the like may be mentioned.

The above mentioned charge transport material may be used either singularly or in combination of two or more kinds.

- As for the resin to be used in the charge transport layer, an insulating resin such as silicon resin, ketone
55 resin, polymethyl methacrylate, polyvinyl chloride, acrylic resin, polyarylate, polyester, polycarbonate,
polystyrene, acrylonitrile-styrene copolymer, acrylonitrile-butadiene copolymer, polyvinyl butylal, polyvinyl
formal, polysulfone polyacrylamide, polyamide, chlorinated rubber or the like; poly-N-vinyl anthracene,
polyvinyl pyrene or the like may be mentioned.

The coating may be applied by means of a method similar to that in the above-mentioned charge generation layer so that a film having a thickness of 5-50 μm preferably 10-20 μm may be formed after drying.

The electrophotographic photosensitive material according to the present invention can be applied not only to a laser beam printer, but also to other various optical memories using light sources in which the wavelength of the light emitted from semiconductor lasers, etc. is 750 to 850 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 and Fig. 2 are partial sectional views of an embodiment of an electrophotographic photosensitive material according to the present invention, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention will be explained in further detail with reference to the embodiments shown in the following working Examples, wherein "parts" means "parts by weight".

Example 1

150 parts of partial N-methoxymethylated amide resin (T-8 manufactured by Yunichika Co., Japan, the degree of substitution of methoxymethyl group - about 31 %) was dissolved in 850 parts of methanol, and was coated on an aluminum plate to obtain a film thickness of 0.2 μm by the use of a dip coating method. After drying at 50 °C for one hour, an undercoat layer was obtained. A solution, in which 4 parts of titanyl phthalocyanine composition crystals (see the above mentioned European Patent Application No. 90 11 0693.0) and 3 parts of a polyvinylbutyral resin were dispersed in 300 parts of THF, was coated on the undercoat layer to obtain a film thickness of 0.2 μm by the use of a dip coating method. After drying at 50 °C for two hours, a charge generation layer was obtained.

Further, a solution, in which 30 parts of p-diethylaminobenzaldehyde-N,N-diphenylhydrazone and 30 parts of a polycarbonate resin (Z-200 manufactured by Mitsubishi Gas chemical Co., Japan) were dissolved in 240 parts of methylene chloride, was coated on the charge generation layer to obtain a film thickness of 15 μm by the use of a dip coating method. After drying at 80 °C for an hour, a charge transport layer was obtained.

In such a way, an electrophotographic photosensitive material having a laminated type photosensitive layer has been obtained. This photosensitive material was measured using an electrostatic copying paper testing apparatus (EPA-8100 manufactured by Kawaguchi Denki Seisakusho, Japan). Namely, the sample was electrified at a dark place by a corona discharge of -5.0 kV to be let alone, and the retention factor of the potential for 5 seconds (v_5/v_0) was measured (V_0 is the initial surface potential and V_5 is the surface potential after 5 seconds). Then, the sample was exposed to a white light of illuminance 5 lux., and the exposure quantity required for attenuating the surface potential to one half ($E_{1/2}$ lux · sec.) was determined. The results of the determination were indicated in Table 1.

Example 2

An electrophotographic photosensitive material was obtained in a manner similar to that of Example 1 except that metal-free phthalocyanine was used as the charge generation substance, and the potential characteristics were examined. The results were indicated in Table 1.

Example 3

An electrophotographic photosensitive material was manufactured in a manner similar to that of Example 1 except that triarylamine was used as the charge transport substance, and the potential characteristics were examined. The results were indicated in Table 1.

Comparative Example 1

An electrophotographic photosensitive material was manufactured in a manner similar to that of Example 1 except that no undercoat layer was used, and the potential characteristics were examined. The results were indicated in Table 1.

Comparative Example 2

An electrophotographic photosensitive material was manufactured in a manner similar to that of Example 1 except that a polycarbonate resin (Z-200 manufactured by Mitsubishi Gas Chemical Co. Japan) was used as the undercoat layer, and the potential characteristics were examined. The results were indicated in Table 1.

Table 1

10

	V_0 (V)	V_5/V_0 (%)	$E_{1/2}$ (lux · s)	V_{res} (V)
Example 1	- 950	93	0.41	3
Example 2	- 970	92	0.81	5
Example 3	- 980	93	0.38	5
Comparative				
Example 1	- 940	75	0.43	5
Comparative				
Example 2	-1020	92	1.1	42

35

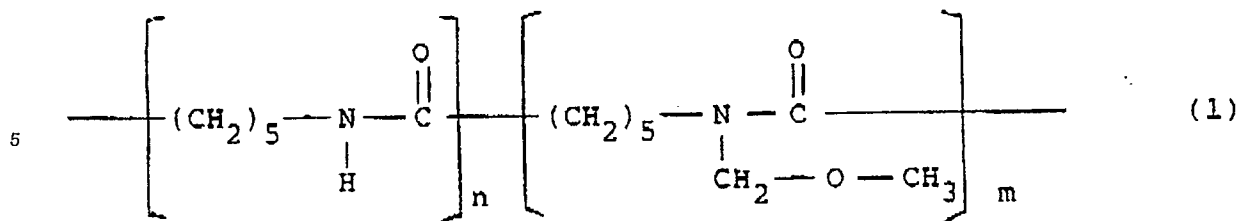
40

- V_0 : surface potential according to a corona discharge (V)
 V_5 : surface potential after 5 seconds (V)
 $E_{1/2}$: exposure quantity required for attenuating surface potential to 1/2 (lux · s)
 V_{res} : residual potential after exposure to light (V)

As explained in detail in the above, according to the present invention, an electrophotographic photosensitive material, which is excellent in the electric chargeability and has high sensitivity, is obtained by using a partial N-methoxymethylation polyamide resin as the undercoat layer of the electrophotographic photosensitive material layer. Thus, an electrophotographic photosensitive material which is very superior in industrial fields, and used in optical printers such as laser beam printers, etc., is obtained.

Claims

1. An electrophotographic photosensitive material comprising an undercoat layer and an electrophotographic photosensitive material layer which are successively laminated on a surface of a conductive substrate, wherein said undercoat layer contains a high molecular substance which is represented by the general formula (1):



10 (wherein m/n represents a real number equal to or larger than 0.1, and n is not zero).

2. The electrophotographic photosensitive material according to claim 1, characterized in that a charge generation material has as the effective components, a composition crystal which contains a total of not more than 50 parts by weight of one or more kinds from among metal-free aza-phthalocyanine porphyrin derivatives, metallo-aza-phthalocyanine porphyrin derivatives, metal-free phthalocyanine, metallo-phthalocyanine, metal-free naphthalocyanine or metallo-naphthalocyanine (wherein metal-free aza-phthalocyanine porphyrin derivatives, metallo-aza-phthalocyanine porphyrin derivatives, metal-free phthalocyanine and metallo-phthalocyanine may have a substitutional group in the benzene nucleus and metal-free naphthalocyanine and metallo-naphthalocyanine may have a substitutional group in the naphthyl nucleus) and 100 parts by weight of titanyl phthalocyanine. and said composition crystal has in its infrared absorption spectrum characteristically strong absorptions at absorption wavelength of $1490 \pm 2 \text{ cm}^{-1}$, $1415 \pm 2 \text{ cm}^{-1}$, $1332 \pm 2 \text{ cm}^{-1}$, $1119 \pm 2 \text{ cm}^{-1}$, $1072 \pm 2 \text{ cm}^{-1}$, $1060 \pm 2 \text{ cm}^{-1}$, $961 \pm 2 \text{ cm}^{-1}$, $893 \pm 2 \text{ cm}^{-1}$, $780 \pm 2 \text{ cm}^{-1}$, $751 \pm 2 \text{ cm}^{-1}$ and $730 \pm 2 \text{ cm}^{-1}$.

FIG. 1

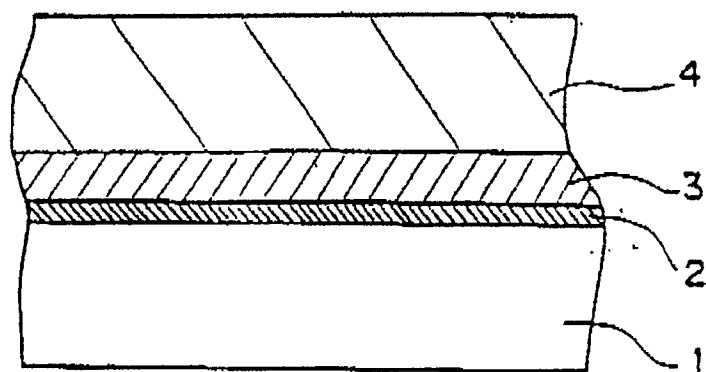
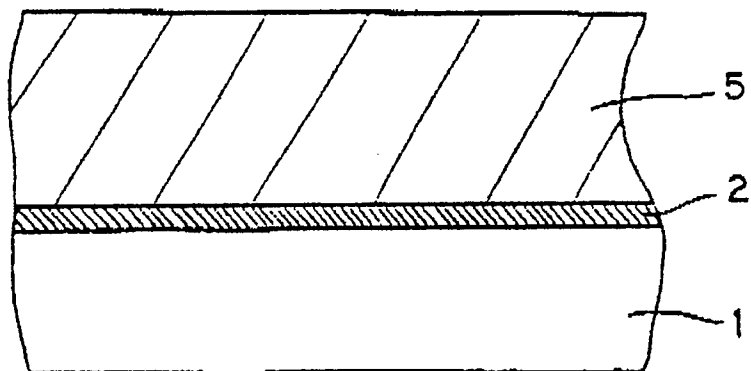


FIG. 2





European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 5260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-3 716 975 (RICOH CO. LTD.) * page 3, lines 29 - 66; claims 1-17 * - - -	1,2	G 03 G 5/14
X	US-A-4 495 263 (EASTMAN KODAK CO.) * column 2, line 63 - column 3, line 23; claims 1-13 * - - -	1	
P,X	EP-A-0 378 153 (KONICA CO.) * page 4, lines 9 - 21; claims 1-18 * - - -	1,2	
P,X	FR-A-2 642 189 (CANON K.K.) * claims 1-5 * - - -	1,2	
X	PATENT ABSTRACTS OF JAPAN vol. 7, no. 196 (P-219)(1341) 26 August 1983, & JP-A-58 95351 (CANON K.K.) 06 June 1983, * the whole document * - - -	1,2	
P,X	DATABASE WPIL, no. 91-121970, Derwent & JP-A-03 62041 (CANON K.K.) 18 March 1991 * whole abstract - - -	1,2	
X	DATABASE WPIL, no. 83-709070, Derwent & JP-A-58 95744 (CANON K.K.) 07 June 1983 * whole abstract - - - - -	1,2	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 10 July 91	Examiner BATTISTIG M.L.A.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document			