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54 **Photosensitive recording material.**

57 A photosensitive recording material which comprises an electrically conductive support having thereon a layer containing a charge transporting compound (n-CTM-compound) capable of accepting and transporting electrons which have been obtained by radiation-activated charge-generation from a charge generating compound (CGM-compound) present in said material, wherein said n-CTM-compound corresponds to general formula (A) defined in the description.

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1. Field of the invention.

The present invention relates to photosensitive recording materials suitable for use in electrophotography.

2. Background of the invention

In electrophotography photoconductive compounds are used to form a latent electrostatic charge image on the surface of a recording material containing such compounds. The latent electrostatic charge image is made visible with a finely divided colouring material, called toner, is transferred to a suitable substrate and is fixed by heat, pressure and/or solvent to said substrate.

The formation of said latent image can proceed by the use in said recording material of so-called charge generating material (CGM) and charge transporting material (CTM) and by a process comprising the following steps :

- surface charging of the earthed photoconductive recording material with either positive or negative charge depending on the composition of the photoconductive recording material;
- imagewise exposure of the photoconductive recording material wherein electron-hole pairs are produced in the charge generating material (CGM) upon absorption of incident light;
- transfer of charge from the imagewise-produced charge carriers (electrons or positive holes) to the charge transporting material (CTM);
- transport of the electrons or holes produced by this process to the surface of the photoconductive recording material under the influence of the electric field applied over said material whereupon discharge of the surface charge takes place.

The photosensitive recording material may incorporate the charge generating material and charge transporting material in separate contacting layers or in a single layer.

To obtain the chargeability required to obtain an adequately toned image the photoconductive layer or layers must have a certain minimum overall thickness, usually at least 10 micron.

It has been found experimentally that, in general, a higher photosensitivity is obtained if most of the overall thickness is occupied by one or more CTM's. In such configurations the layer in which charge generation or combined charge generation and charge transport take place and which largely determines the photosensitivity of the photosensitive recording material is fairly thin, with a thickness between 0.3 and 5 microns. Abrasion of this layer would immediately lead to a significant reduction in photosensitivity, which is undesirable.

High sensitivity photoconductive recording materials have therefore, in general, the layer whose sole function is charge transport as an outermost layer and a fairly thin charge generation material layer or layer of combined charge generation-charge transport material between the charge transporting layer and a conductive base serving as contacting electrode. In such configurations the sign of the electrostatic chargeability of the photosensitive recording material will depend upon whether the CTM or CTM's in the charge transporting layer preferentially transport electrons or positive holes. In the case of hole-transport the photosensitive recording material will be negatively chargeable and in the case of electron transport the photosensitive recording material will be positively chargeable.

Patent literature in the field frequently deals with hole-transporting CTM's, but little literature is available concerning electron-transporting CTM's. The scarcity of efficient electron-transporting CTM's is underlined by the predominance of negatively chargeable organic photoconductors (OPC's) in the commercially available photoconductive recording systems.

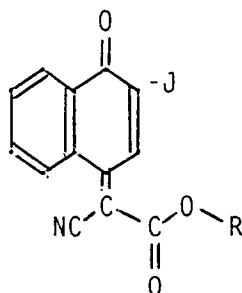
There are, however, applications in which it is more desirable to charge the photosensitive recording material positively rather than negatively, e.g. because of the availability of a better positively chargeable or negatively chargeable toner, depending on whether toner development proceeds in a negative-positive process or positive-positive (reversal) process.

A search has revealed that only a small number of efficient and practically useful electron transporting materials, called n-CTM's, are available because of the following problems :

- insufficient solubility in binders and coating solvents
- toxicity
- fatigue effects
- intrinsic colour

One of the most efficient n-CTM's is 2,4,7-trinitrofluorenone (TNF) disclosed in US-P 3,484,237. However, TNF is carcinogenic and has an intensive yellow colour, which disqualifies it from applications with a light source from the short wavelength end of the visible spectrum.

In US-P 4,869,985 n-CTM compounds within the scope of the following general formula have been disclosed :



wherein :

J is alkyl having 1 to 6 carbon atoms, and

R is normal alkyl having 1 to 6 carbon atoms.

In this patent it is stated that these compounds exhibit good solubility or dispersibility in many coating solvents and in many film-forming binders.

They have a good capability of accepting and transporting electrons generated by radiation-activated charge-generation materials (CGM's), and they do not impart unacceptably high dark decay properties to electrophotographic recording elements.

As can be derived from the US-P and prior art discussed therein it is rather difficult to find electron-transporting compounds (n-CTM's) with adequate solubility in casting solvents and binders.

Further an efficient electron transporting compound in a photosensitive recording material must exhibit :

- a reduction potential which enables efficient electron transfer to take place between the CGM and the n-CTM;
- chemical stability;
- acceptable electro-optical stability in electro-optical cycling; and
- efficient electron transport.

3. Summary of the invention

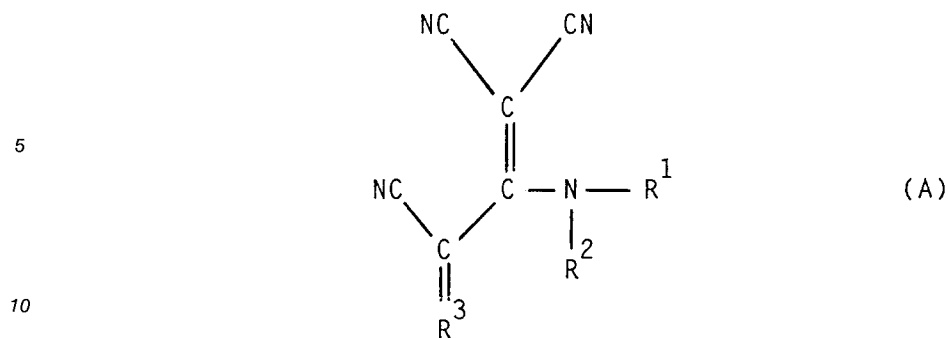
It is an object of the present invention to provide electron-transporting compounds called n-CTM's for use in photosensitive recording materials having :

- (1) excellent solubility in casting solvents such as methylene chloride; and
- (2) excellent solubility in binders such as polycarbonate and polystyrene in the absence of p-CTM's.

It is a further object to provide electrophotographic printing materials suitable for use with laser or LED light sources which materials incorporate said CTM's and which are characterized by high photosensitivity, high charging level and low fatigue (i.e. charging level and residual potential stability) in cyclic use.

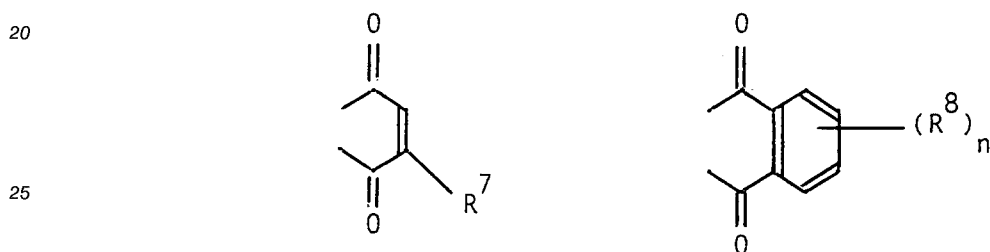
Other objects and advantages of the present invention will appear from the further description and examples.

In accordance with the present invention a photosensitive recording material is provided which comprises an electrically conductive support having thereon a layer containing a charge transporting compound (n-CTM-compound) capable of accepting and transporting electrons which have been obtained by radiation-activated charge-generation from a charge generating compound (CGM-compound) present in said material, characterized in that said n-CTM-compound corresponds to the following general formula (A) :

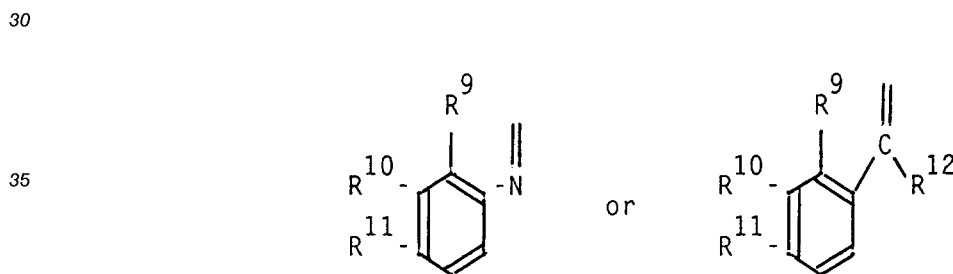


wherein :

each of R^1 and R^2 (same or different) represents an alkyl group including a substituted alkyl group, a
 15 cycloalkyl group including a substituted cycloalkyl group, an aryl group including a substituted aryl group,
 COOR^4 , COR^4 , CSR^4 , POR^4R^5 , SO_2R^6 , or together form a member selected from the group consisting of :



R^3 represents



each of R^4 , R^5 and R^7 independently represents an alkyl, aryl or aralkyl group;

R^6 represents an alkyl, aryl, aralkyl group, F or Cl;

R^8 represents an alkyl, aryl, aralkyl, alkoxy, COR^4 , COOR^4 , CN, NO_2 , F, Cl or SO_2R^6 ;

R^9 represents hydrogen, NHCOR^4 , $\text{NHCO}(\text{CH}_3)=\text{CH}_2$, NHCOOR^4 , alkyl, alkoxy or R^9 and R^{10} represent
 45 together the necessary atoms to close a carbocyclic or heterocyclic adjacent ring;

R^{11} represents hydrogen, alkyl, aryl, aralkyl, alkoxy, COR^4 , COOR^4 , CN, NO_2 , F, Cl, SO_2R^6 or $\text{NR}^{13}\text{R}^{14}$;

R^{12} represents hydrogen, alkyl, aryl, alkoxy, CN, NO_2 , F, Cl, COR^4 , COOR^4 or SO_2R^6 ;

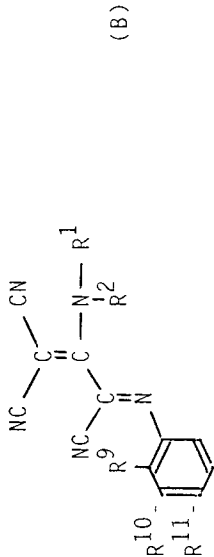
each of R^{13} and R^{14} independently represents an alkyl group, an aryl group, COOR^4 or COR^4 ;

$n = 0, 1$ or 2 .

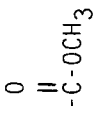
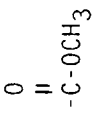
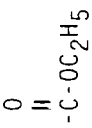
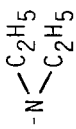
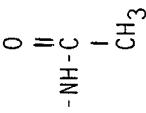
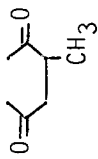
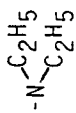
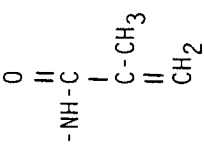
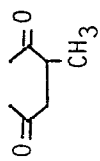
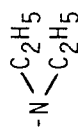
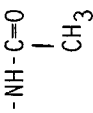
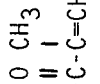
4. Detailed description of the invention

Particularly suitable compounds for use according to the present invention are within the scope of
 55 general formula (B) of the following Table 1, listing also the melting points, solubility in CH_2Cl_2 , half-wave
 reduction potentials, and their longest wavelength absorption maximum :

Table 1

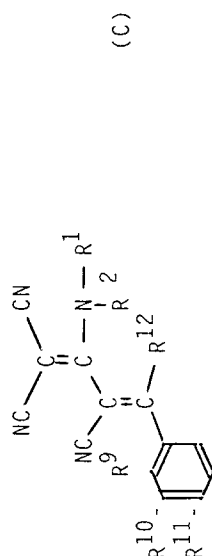


No. R ¹	R ²	R ⁹	R ¹⁰	R ¹¹	Melting point [°C]	¹ / ₂ E _{red} [V]	Solubility in CH ₂ Cl ₂ g/100 ml	Longest wave-length λ _{max} [nm]
1	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-OC}_4\text{H}_9 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-NH-C} \\ \\ \text{CH}_3 \end{array}$	H	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{-N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_5 \end{array}$	102	-0.280	15 to 20	613
2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-COCH}_2\text{CH} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{-NHC=O} \\ \\ \text{CH}_3 \end{array}$	H	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{-N} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_5 \end{array}$	127	-0.280	40 to 45	647

	5	10	15	20	25	30	35	40	45
3		-0.095	129	H	H	H			
4		-0.140	73	H	H	CH ₃			
5		-0.110	90	H	H	H			
6		-0.210	189		H				
7		-0.265	171		H				
8		-0.353	208		H				

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Table 2



No.	R ¹	R ²	R ⁹	R ¹⁰	R ¹¹	R ¹²	Melting point [°C]	E _{red} ^{1/2} [V]	Solubility in CH ₂ Cl ₂ g/100 ml	Longest wave- length λ _{max} [nm]
13			H	H	-N< C ₂ H ₅ C ₂ H ₅	CN	250-260	-0.178	5 to 10	620
14			H	H	-N< C ₂ H ₅ C ₂ H ₅	H	220	-0.698	5 to 10	549

The preparation of compounds according to general formula (A) is described in published European Patent Application 0 400 706.

According to an embodiment an electrophotographic recording material of the present invention comprises an electrically conductive support having thereon a photosensitive charge generating layer in contiguous relationship with a charge transporting layer, characterized in that said charge transporting layer

contains one or more n-CTM compounds corresponding to a general formula (A) as defined above.

The content of the n-CTM compound used according to the present invention in a negative charge transport layer is preferably in the range of 20 to 70 % by weight with respect to the total weight of said layer. The thickness of the charge transporting layer is preferably in the range of 5 to 50 μm , and more preferably in the range of 5 to 30 μm .

According to another embodiment an electrophotographic recording material of the present invention comprises an electrically conductive support having thereon a positively chargeable photoconductive recording layer which contains in an electrically insulating organic polymeric binder at least one p-type pigment substance and at least one n-type photoconductive charge transport substance, wherein (i) at least one of the n-type charge transport substances is a compound corresponding to general formula (A) as defined above, (ii) said layer has a thickness in the range of 4 to 40 μm and comprises 5 to 40 % by weight of said p-type pigment substance and 0.0001 to 15 % by weight of at least one of said n-type charge transport substance(s) that is (are) molecularly distributed in said electrically insulating organic polymeric binder material that has a volume resistivity of at least 10^{14} Ohm-m, and wherein (iii) said recording layer in electrostatically charged state requires for 10 % and 90 % discharge respectively exposures to conductivity increasing electromagnetic radiation that differ by a factor 4.5 or less.

The p-type pigment may be inorganic or organic and may have any colour including white. It is a finely divided substance dispersible in the organic polymeric binder of said photoconductive recording layers.

Optionally the support of said photoconductive recording layer is pre-coated with an adhesive and/or a blocking layer (rectifier layer) reducing or preventing charge injection from the conductive support into the photoconductive recording layer, and optionally the photoconductive recording layer is overcoated with an outermost protective layer, more details about said layers being given furtheron.

In accordance with a preferred mode of said last mentioned embodiment said photoconductive recording layer has a thickness in the range of 5 to 35 μm and contains 6 to 30 % by weight of said p-type pigment material(s) and 0.001 to 12 % by weight of said n-type transport substance(s).

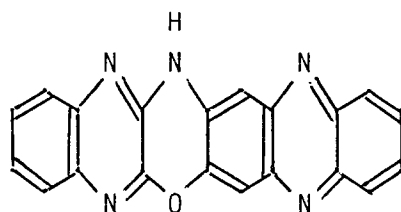
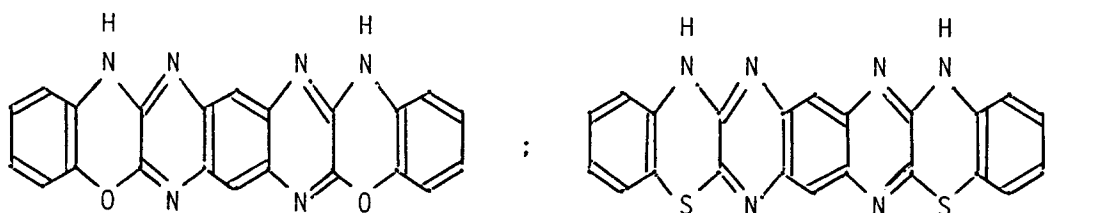
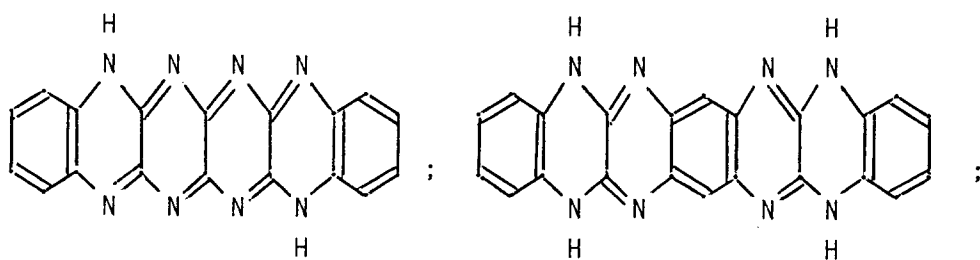
By the term "n-type" material is understood a material having n-type conductance, which means that the photocurrent (I_n) generated in said material when in contact with an illuminated transparent electrode having negative electric polarity is larger than the photocurrent (I_p) generated when in contact with a positive illuminated electrode ($I_n/I_p > 1$).

By the term "p-type" material is understood a material having p-type conductance, which means that the photocurrent (I_n) generated in said material when in contact with an illuminated transparent electrode having positive electric polarity is larger than the photocurrent (I_p) generated when in contact with a negative illuminated electrode ($I_p/I_n > 1$).

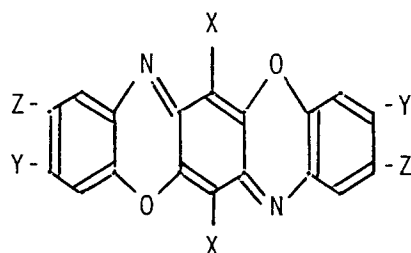
Preferred examples of p-type pigments dispersible in the binder of a negatively chargeable recording layer of the electrophotographic recording material according to said last mentioned preferred embodiment are organic pigments from one of the following classes :

a) naphthalo- and phthalo-cyanines such as metal free, metal, metal-oxy, metal-halo and siloxy-silicon metal naphthalo- and phthalocyanines e.g. χ -metal-free phthalocyanines as described e.g. in US-P 3,594,163; US-P 3,816,118; US-P 3,894,868 and CA-P 899,870; siloxy-silicon naphthalocyanines as described e.g. in EP-A 243,205; vanadyl phthalocyanines as described e.g. in US-P 4,771,133; bromoindium phthalocyanines as described e.g. in US-P 4,666,802 and 4,727,139; τ - and η -metal-free phthalocyanines as described e.g. in US-P 4,749,637 and metal, metal-oxy and metal-halo naphthalocyanines as described e.g. in EP 288,876.

b) quinoxaline pigments e.g.

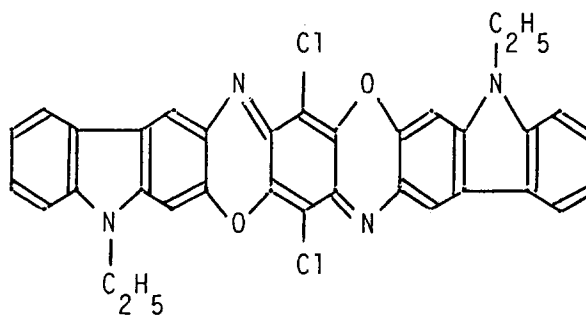


c) dioxazine pigments with the general formula :



wherein

- 45
- X is Cl, CONHC_6H_5 , NHOCCH_3 , NHC_6H_5 , CONH_2 ;
 - Y is p-chlorophenyl, NHC_6H_5 , NHOCCH_3 , NH_2 , OC_6H_5 , H;
 - Z is H, alkoxy, e.g. OC_2H_5 or O-iso. C_3H_7 , Cl, NO_2 or COC_6H_5 ;
 - or Z and Y together form a substituted or unsubstituted heterocyclic ring, e.g.;
- 50
- Carbazole Dioxazine Violet (CI Pigment Violet 23, CI 51319) with the formula :
- 55



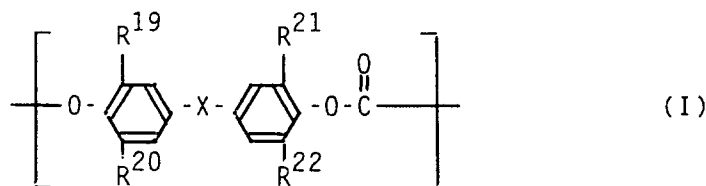
d) p-type polyazo pigments including bisazo-, trisazo- and tetrakisazo-pigments, e.g. the polyazo compounds described in published European Patent Application 0,350,984.

For the production of a preferred recording material according to the present invention at least one of the n-CTM compounds according to the above defined general formula (A) is applied in combination with a resin binder to form a charge transporting layer adhering directly to a charge generating layer on an electrically conductive support. Through the resin binder the charge transporting layer obtains sufficient mechanical strength and obtains or retains sufficient capacity to hold an electrostatic charge for copying purposes. Preferably the specific resistivity of the charge transporting layer is not lower than 10^9 ohm.cm. The resin binders are selected with the aim of obtaining optimal mechanical strength, adherence to the charge generating layer and favourable electrical properties.

Suitable electronically inactive binder resins for use in the charge transporting layer are e.g. cellulose esters, acrylate and methacrylate resins, e.g. cyanoacrylate resin, polyvinyl chloride, copolymers of vinyl chloride, e.g. copolyvinyl/acetate and copolyvinyl/maleic anhydride, polyester resins, e.g. copolyesters of isophthalic acid and terephthalic acid with glycol, aromatic polycarbonate resins and polyester carbonate resins.

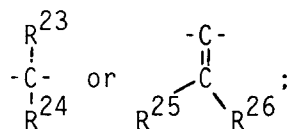
A polyester resin particularly suited for use in combination with aromatic polycarbonate binders is DYNAPOL L 206 (registered trade mark of Dynamit Nobel for a copolyester of terephthalic acid and isophthalic acid with ethylene glycol and neopentyl glycol, the molar ratio of tere- to isophthalic acid being 3/2). Said polyester resin improves the adherence to aluminium that may form a conductive coating on the support of the recording material.

Suitable aromatic polycarbonates can be prepared by methods such as those described by D. Freitag, U. Grigo, P. R. Müller and W. Nouvertné in the Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol. II, pages 648-718, (1988) published by Wiley and Sons Inc., and have one or more repeating units within the scope of following general formula (I) :



wherein :

X represents S, SO₂,

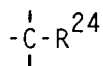


R¹⁹, R²⁰, R²¹, R²², R²⁵ and R²⁶ each represents (same or different) hydrogen, halogen, an alkyl group or an aryl group, and

R²³ and R²⁴ each represent (same or different) hydrogen, an alkyl group, an aryl group or together represent the necessary atoms to close a cycloaliphatic ring, e.g. cyclohexane ring.

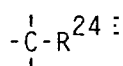
Aromatic polycarbonates having a molecular weight in the range of 10,000 to 200,000 are preferred. Suitable polycarbonates having such a high molecular weight are sold under the registered trade mark MAKROLON of Farbenfabriken Bayer AG, W-Germany.

MAKROLON CD 2000 (registered trade mark) is a bisphenol A polycarbonate with molecular weight in the range of 12,000 to 25,000 wherein $R^{19} = R^{20} = R^{21} = R^{22} = H$, X is R^{23}



10 with $R^{23} = R^{24} = \text{CH}_3$.

MAKROLON 5700 (registered trade mark) is a bisphenol A polycarbonate with molecular weight in the range of 50,000 to 120,000 wherein $R^{19} = R^{20} = R^{21} = R^{22} = H$, X is R^{23}

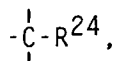


15

with $R^{23} = R^{24} = \text{CH}_3$.

Bisphenol Z polycarbonate is an aromatic polycarbonate containing recurring units wherein $R^{19} = R^{20} = R^{21} = R^{22} = H$, X is R^{23}

20



and R^{23} together with R^{24} represents the necessary atoms to close a cyclohexane ring.

25 Further useful binder resins are silicone resins, polystyrene and copolymers of styrene and maleic anhydride and copolymers of butadiene and styrene.

An example of an electronically active resin binder is poly-N-vinylcarbazole or copolymers of N-vinylcarbazole having a N-vinylcarbazole content of at least 40 % by weight.

30 The ratio wherein the charge-transporting compound and the resin binder are mixed can vary. However, relatively specific limits are imposed, e.g. to avoid crystallization.

The presence of one or more spectral sensitizing agents can have an advantageous effect on the charge transport. In that connection reference is made to the methine dyes and xanthene dyes described in US-P 3,832,171. Preferably these dyes are used in an amount not substantially reducing the transparency in the visible light region (420 - 750 nm) of the charge transporting layer so that the charge generating layer still can receive a substantial amount of the exposure light when exposed through the charge transporting layer.

35 The charge transporting layer may contain compounds substituted with electron-donor groups forming an intermolecular charge transfer complex, i.e. donor-acceptor complex wherein the hydrazone compound represents an electron donating compound. Useful compounds having electron-donating groups are hydrazones such as 4-N,N-diethylamino-benzaldehyde-1,1-diphenylhydrazone (DEH), amines such as tris(p-tolylamine) (TTA) and N,N'-diphenyl-N,N'-bis(3-methyl-phenyl)-[1,1-biphenyl]-4,4'-diamine (TPD) etc. The optimum concentration range of said compounds is such that the molar donor/acceptor ratio is 10 : 1 to 1,000 : 1 and vice versa.

45 Compounds acting as stabilising agents against deterioration by ultra-violet radiation, so-called UV-stabilizers, may also be incorporated in said charge transport layer. Examples of UV-stabilizers are benztriazoles.

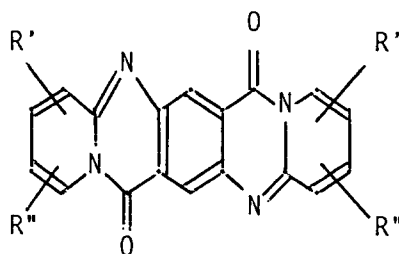
For controlling the viscosity of the coating compositions and controlling their optical clarity silicone oils may be added to the charge transport layer.

50 The charge transport layer used in the recording material according to the present invention possesses the property of offering a high charge transport capacity coupled with a low dark discharge. While with the common single layer photoconductive systems an increase in photosensitivity is coupled with an increase in the dark current and fatigue such is not the case in the double layer arrangement wherein the functions of charge generation and charge transport are separated and a photosensitive charge generating layer is arranged in contiguous relationship to a charge transporting layer.

55 As charge generating compounds for use in a recording material according to the present invention any of the organic pigment dyes belonging to one of the following classes and able to transfer electrons to electron transporting materials may be used :

a) perylamides, e.g. C.I. 71 130 (C.I. = Colour Index) described in DBP 2,237,539,

- b) polynuclear quinones, e.g. anthanthrones such as C.I. 59 300 described in DBP 2,237,678,
 c) quinacridones, e.g. C.I. 46 500 described in DBP 2,237,679,
 d) naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, e.g. Orange GR, C.I. 71 105 described in DBP 2,239,923,
 5 e) phthalocyanines and naphthalocyanines, e.g. H₂-phthalocyanine in X-crystal form (X-H₂Pc), metal phthalocyanines, e.g. CuPc C.I. 74 160 described in DBP 2 239 924, indium phthalocyanine described in US-P 4,713,312, and silicon naphthalocyanines having siloxy groups bonded to the central silicon as described in EP-A 0243 205.
 f) indigo- and thioindigo dyes, e.g. Pigment Red 88, C.I. 73 312 described in DBP 2 237 680,
 10 g) benzothioxanthene-derivatives as described e.g. in DAS 2 355 075,
 h) perylene 3,4,9,10-tetracarboxylic acid derived pigments including condensation products with o-diamines as described e.g. in DAS 2 314 051,
 i) polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, e.g. Chlordiane Blue C.I. 21 180 described in DAS 2 635 887, and bisazopigments described in DOS 2 919 791, DOS 3 026 653 and
 15 DOS 3 032 117,
 j) squarilium dyes as described e.g. in DAS 2 401 220,
 k) polymethine dyes.
 l) dyes containing quinazoline groups, e.g. as described in GB-P 1,416,602 according to the following general formula :



20
 25
 30 Inorganic substances suited for photogenerating negative charges in a recording material according to the present invention are e.g. amorphous selenium and selenium alloys e.g. selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic and inorganic photoconductive crystalline compounds such as cadmium sulphoselenide, cadmiumselenide, cadmium sulphide and mixtures thereof as disclosed in US-P
 35 4,140,529.

Said photoconductive substances functioning as charge generating compounds may be applied to a support with or without a binding agent. For example, they are coated by vacuum-deposition without binder as described e.g. in US-P 3,972,717 and 3,973,959. When dissolvable in an organic solvent the photoconductive substances may likewise be coated using a wet coating technique known in the art whereupon the
 40 solvent is evaporated to form a solid layer. When used in combination with a binding agent or agents at least the binding agent(s) should be soluble in the coating solution and the charge generating compound dissolved or dispersed therein. The binding agent(s) may be the same as the one(s) used in the charge transport layer which normally provides best adhering contact. In some cases it may be advantageous to use in one or both of said layers a plasticizing agent, e.g. halogenated paraffin, polybiphenyl chloride,
 45 dimethylnaphthalene or dibutyl phthalate.

The thickness of the charge generating layer is preferably not more than 10 μm , more preferably not more than 5 μm .

In the recording materials of the present invention an adhesive layer or barrier layer may be present between the charge generating layer and the support or the charge transport layer and the support. Useful
 50 for that purpose are e.g. a polyamide layer, nitrocellulose layer, hydrolysed silane layer, or aluminium oxide layer acting as blocking layer preventing positive or negative charge injection from the support side. The thickness of said barrier layer is preferably not more than 1 micron.

The conductive support may be made of any suitable conductive material. Typical conductors include aluminum, steel, brass and paper and resin materials incorporating or coated with conductivity enhancing
 55 substances, e.g. vacuum-deposited metal, dispersed carbon black, graphite and conductive monomeric salts or a conductive polymer, e.g. a polymer containing quaternized nitrogen atoms as in Calgon Conductive polymer 261 (trade mark of Calgon Corporation, Inc., Pittsburgh, Pa., U.S.A.) described in US-P 3,832,171.

The support may be in the form of a foil, web or be part of a drum.

An electrophotographic recording process according to the present invention comprises the steps of :

(1) overall charging, e.g. with corona-device, the photoconductive layer containing at least one n-CTM compound according to the general formula (A);

(2) image-wise photo-exposing said layer thereby obtaining a latent electrostatic image, that may be toner-developed.

When applying a bilayer-system electrophotographic recording material including on an electrically conductive support a photosensitive charge generating layer in contiguous relationship with a charge transporting layer that contains one or more n-CTM compounds corresponding to the general formula (A) as defined above, the photo-exposure of the charge generating layer proceeds preferably through the charge transporting layer but may be direct if the charge generating layer is uppermost or may proceed likewise through the conductive support if the latter is transparent enough to the exposure light.

The development of the latent electrostatic image commonly occurs preferably with finely divided electrostatically attractable material, called toner particles that are attracted by coulomb force to the electrostatic charge pattern. The toner development is a dry or liquid toner development known to those skilled in the art.

In positive-positive development toner particles deposit on those areas of the charge carrying surface which are in positive-positive relation to the original image. In reversal development, toner particles migrate and deposit on the recording surface areas which are in negative-positive image value relation to the original. In the latter case the areas discharged by photo-exposure obtain by induction through a properly biased developing electrode a charge of opposite charge sign with respect to the charge sign of the toner particles so that the toner becomes deposited in the photo-exposed areas that were discharged in the imagewise exposure (ref. : R.M. Schaffert "Electrophotography" - The Focal Press - London, New York, enlarged and revised edition 1975, p. 50-51 and T.P. Maclean "Electronic Imaging" Academic Press - London, 1979, p. 231).

According to a particular embodiment electrostatic charging, e.g. by corona, and the imagewise photo-exposure proceed simultaneously.

Residual charge after toner development may be dissipated before starting a next copying cycle by overall exposure and/or alternating current corona treatment.

Recording materials according to the present invention depending on the spectral sensitivity of the charge generating layer may be used in combination with all kinds of photon-radiation, e.g. light of the visible spectrum, infra-red light, near ultra-violet light and likewise X-rays when electron-positive hole pairs can be formed by said radiation in the charge generating layer. Thus, they can be used in combination with incandescent lamps, fluorescent lamps, laser light sources or light emitting diodes by proper choice of the spectral sensitivity of the charge generating substance or mixtures thereof.

The toner image obtained may be fixed onto the recording material or may be transferred to a receptor material to form thereon after fixing the final visible image.

A recording material according to the present invention showing a particularly low fatigue effect can be used in recording apparatus operating with rapidly following copying cycles including the sequential steps of overall charging, imagewise exposing, toner development and toner transfer to a receptor element.

The following examples further illustrate the present invention. All parts, ratios and percentages are by weight unless otherwise stated.

The evaluations of electrophotographic properties determined on the recording materials of the following examples relate to the performance of the recording materials in an electrophotographic process with a reusable photoreceptor. The measurements of the performance characteristics were carried out by using a sensitometric measurement in which the discharge was obtained for 8 different exposures including zero exposure. The photoconductive recording sheet material was mounted with its conductive backing on an aluminium drum which was earthed and rotated at a circumferential speed of 5 cm/s. The recording material was sequentially charged with a corona at a voltage of -4.3 kV or +4.3 kV operating with a corona current of about 1 μ A per cm of corona wire. Subsequently the recording material was exposed (simulating image-wise exposure) with a light dose of monochromatic light obtained from a monochromator positioned at the circumference of the drum at an angle of 45° with respect to the corona source. The photo-exposure lasted 400 ms. Thereupon, the exposed recording material passed an electrometer probe positioned at an angle of 180° with respect to the corona source. After effecting an overall post-exposure with a halogen lamp producing 54.000 mJ/m² positioned at an angle of 270° with respect to the corona source a new copying cycle started. Each measurement relates to 40 copying cycles in which the photoconductor is exposed to the full light source intensity for the first 5 cycles, then sequentially to the light source the light output of which is moderated by grey filters of optical densities 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 each for 5 cycles

and finally to zero light intensity for the last 5 cycles.

The electro-optical results quoted in the EXAMPLES 1 to 6 hereinafter refer to charging level at zero light intensity (CL) and to discharge at a light intensity corresponding to the light source intensity moderated by a grey filter with an optical density of 1.0 to a residual potential RP except in the case of 780 nm exposure in which the grey filter has an optical density of 1.5.

The % discharge is :

$$\frac{(CL-RP)}{CL} \times 100$$

For a given corona voltage, corona current, separating distance of the corona wires to recording surface and drum circumferential speed the charging level CL is only dependent upon the thickness of the charge transport layer and its specific resistivity. In practice CL expressed in volts should be preferably ≥ 30 d, where d is the thickness in μm of the charge transport layer.

The half-wave reduction potential measurements were carried out using a polarograph with rotating (500 rpm) disc platinum electrode and standard saturated calomel electrode at room temperature (20 °C) using a product concentration of 10^{-4} mole and an electrolyte (tetrabutylammonium perchlorate) concentration of 0.1 mole in spectroscopic grade acetonitrile. Ferrocene was used as a reference substance having a half-wave oxidation potential of +0.430 V.

All ratios and percentages mentioned in the Examples are by weight.

EXAMPLES 1 to 13

A photoconductor sheet was produced by first doctor blade coating a 100 μm thick polyester film pre-coated with a vacuum-deposited conductive layer of aluminium with a 1 % solution of γ -aminopropyltriethoxy silane in aqueous methanol. After solvent evaporation and curing at 100 °C for 30 minutes, the thus obtained adhesion/blocking layer was doctor blade coated with a dispersion of charge generating pigment to thickness of 0.6 micron.

Said dispersion was prepared by mixing 5 g of the χ -form of purified metal-free phthalocyanine, 5 g of aromatic polycarbonate MAKROLON CD 2000 (registered trade mark) and 132.86 g of dichloromethane for 16 hours in a ball mill. Subsequently 23.81 g of dichloromethane was added to the dispersion to produce the composition and viscosity for coating.

After drying for 15 minutes at 50 °C, strips of said supported layer were coated with a filtered solution of charge transporting material as defined hereinafter in Table 3 and MAKROLON 5700 (registered trade mark) in dichloromethane at a solids content of 12 % by wt. The coated layers were dried at 50 °C for 16 hours.

The characteristics of the thus obtained photoconductive recording materials were determined with light doses and at the wavelengths given in Table 3 below.

The n-CTM-concentrations in the charge transport layers of Examples 1 to 12 are given in Table 3.

The charging level (CL) expressed in volt [V], received exposure dose (It), and the residual potential (RP) and % discharge of each recording material are also given in Table 3.

TABLE 3

Example No.	Charge trans-port comp.	Charge transp. comp. conc. % wt	Thick. of CTL μm	Wave-length [nm]	CL [V]	Exposure It [mJ/m ²]	RP [V]	% discharge
1	1	50	12.4	780	+ 565	20.7	+ 102	81.9
2	2	50	14.4	780	+ 527	20.7	+ 114	78.4
3	3	50	12.4	650	+ 573	20	+ 395	31.1
4	4	50	13.4	780	+ 1250	20.7	+ 891	28.7
5	5	50	10.4	650	+ 575	20	+ 404	29.7
6	6	50	14.4	780	+ 378	20	+ 182	51.9
7	7	50	10.4	780	+ 450	20	+ 246	45.3
8	8	50	12.4	780	+ 436	20	+ 251	42.4
9	9	50	12.4	780	+ 470	20	+ 274	41.7
10	10	50	13.4	780	+ 1349	20.7	+ 1113	17.5
11	11	50	12.4	780	+ 394	20	+ 145	63.2
12	12	50	11.4	780	+ 556	20	+ 372	33.1
13	12	50	10.4	780	+ 838	20	+ 631	24.7

EXAMPLES 14 to 25

The photoconductive recording materials of Examples 14 to 25 were produced as for Examples 1 to 13 except that the adhesion/blocking layer was produced by coating the aluminium-coated polyester film with a 3 % solution of γ -aminopropyltriethoxysilane in aqueous methanol instead of a 1 % solution, the ω -form of metal-free triazatetrabenzoporphine (already described in unpublished EP-A 89121024.7) was applied at a concentration of 40 % in the charge generating layer instead of the χ -form of metal-free phthalocyanine at a concentration of 50 % by weight.

The characteristics of the thus obtained photoconductive recording material were determined as described above but with photo-exposure to the light doses and at the wavelengths given in Table 4 below.

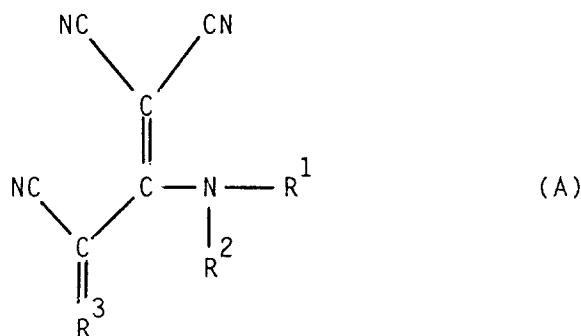
The charge transport compounds used, their concentration in the charge transport layer, the thickness in μm of the charge transport layer (CTL) and the electro-optical characteristics of the corresponding photoconductive recording materials are summarized in said Table 4.

TABLE 4

Example No.	Charge trans-port comp.	Charge transp. comp. conc. % wt	Thick. of CTL μm	Wave-length [nm]	CL [V]	Exposure It [mJ/m ²]	RP % [V]	discharge
14	1	50	11.4	780	+ 405	20.7	+ 155	61.7
15	2	50	13.4	780	+ 310	20.7	+ 128	58.7
16	3	50	11.4	650	+ 485	20	+ 400	17.5
17	4	50	11.4	780	+ 1148	20.7	+ 834	27.4
18	5	50	13.4	650	+ 526	20	+ 464	11.8
19	6	50	13.4	780	+ 275	20	+ 209	24.0
20	7	50	15.4	780	+ 471	20	+ 315	33.1
21	8	50	13.4	780	+ 514	20	+ 427	16.9
22	9	50	14.4	780	+ 439	20	+ 280	36.2
23	10	50	13.1	780	+ 1331	20.7	+ 1095	17.7
24	11	50	13.4	780	+ 400	20	+ 234	41.5
25	12	50	12.4	780	+ 535	20	+ 433	19.1

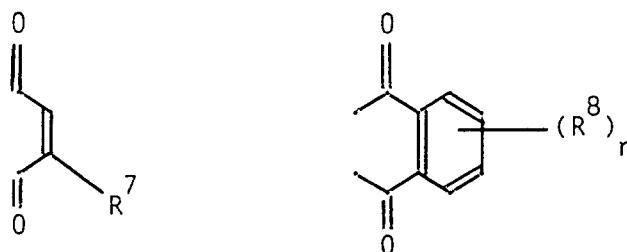
Claims

1. A photosensitive recording material which comprises an electrically conductive support having thereon a layer containing a charge transporting compound (n-CTM-compound) capable of accepting and transporting electrons which have been obtained by radiation-activated charge-generation from a charge generating compound (CGM-compound) present in said material, characterized in that said n-CTM-compound corresponds to the following general formula (A) :

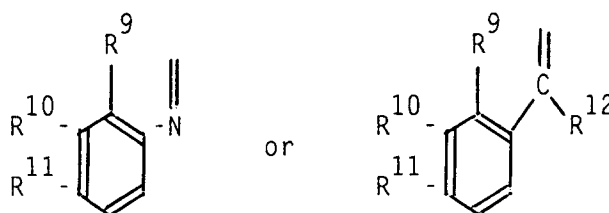


wherein :

each of R¹ and R² (same or different) represents an alkyl group including a substituted alkyl group, a cycloalkyl group including a substituted cycloalkyl group, an aryl group including a substituted aryl group, COOR⁴, COR⁴, CSR⁴, POR⁴R⁵, SO₂R⁶, or together form a member selected from the group consisting of :



R³ represents



each of R⁴, R⁵ and R⁷ independently represents an alkyl, aryl or aralkyl group;

R⁶ represents an alkyl, aryl, aralkyl group, F or Cl ;

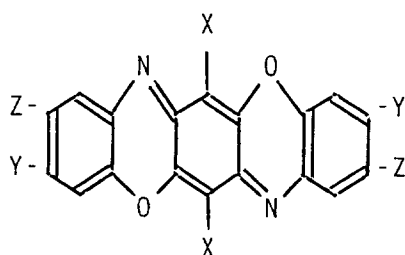
R⁸ represents an alkyl, aryl, aralkyl, alkoxy, COR⁴, COOR⁴, CN, NO₂, F, Cl or SO₂R⁶ group;

R⁹ represents hydrogen, NHCOR⁴, NHCO(CH₃)=CH₂, NHCOR⁴, alkyl, alkoxy or R⁹ and R¹⁰ represent together the necessary atoms to close a carbocyclic or heterocyclic adjacent ring;

R¹¹ represents hydrogen, alkyl, aryl, aralkyl, alkoxy, COR⁴, COOR⁴, CN, NO₂, F, Cl, SO₂R⁶ or NR¹³R¹⁴ group;

R^{12} represents hydrogen, alkyl, aryl, alkoxy, CN, NO_2 , F, Cl, COR^4 , $COOR^4$ or SO_2R_6 group; each of R^{13} and R^{14} independently represents an alkyl group, an aryl group, $COOR^4$ or COR^4 ; and n represents zero, 1 or 2.

2. Photosensitive recording material according to claim 1, wherein said CGM-compound is present in a photosensitive charge generating layer and said n-CTM compound is present in a charge transporting layer that stands in direct contact with said charge generating layer.
3. Photosensitive recording material according to claim 1, wherein said conductive support stands in contact with a positively chargeable photoconductive recording layer which contains in an electrically insulating organic polymeric binder at least one photoconductive p-type pigment substance and at least one n-type charge transport substance, wherein (i) said n-type charge transport substance is a n-CTM compound corresponding to said general formula (A), (ii) said recording layer has a thickness in the range of 4 to 40 μm and comprises 5 to 40 % by weight of said p-type pigment substance and 0.0001 to 15 % by weight of at least one of said n-type charge transport substance(s) that is (are) molecularly distributed in said electrically insulating organic polymeric binder material that has a volume resistivity of at least 10^{14} Ohm-m, and (iii) said recording layer in electrostatically charged state requires for 10 % and 90 % discharge respectively exposures to conductivity increasing electromagnetic radiation that differ by a factor 4.5 or less.
4. Photosensitive recording material according to claim 3, wherein said photoconductive recording layer has a thickness in the range of 5 to 35 μm and contains 6 to 30 % by weight of at least one of said p-type pigment substances and 0.001 to 12 % by weight of at least one of said n-type transport substances.
5. Photosensitive recording material according to claim 3 or 4, wherein said p-type pigment substance is an organic pigment from one of the following classes :
 - a) naphthalo- and phthalo-cyanines such as metal free, metal, metal-oxy, metal-halo and siloxy-silicon metal naphthalo- and phthalocyanines,
 - b) quinoxaline pigments,
 - c) dioxazine pigments with the general formula :



wherein

- X is Cl, $CONHC_6H_5$, $NHOCCH_3$, NHC_6H_5 , $CONH_2$;
 Y is p-chlorophenyl, NHC_6H_5 , $NHOCCH_3$, NH_2 , OC_6H_5 , H;
 Z is H, alkoxy, e.g. OC_2H_5 or O-iso. C_3H_7 , Cl, NO_2 or COC_6H_5 ;
 or Z and Y together form a substituted or unsubstituted heterocyclic ring,
 d) p-type polyazo pigments including bisazo-, trisazo- and tetrakisazo-pigments.

6. Photosensitive recording material according to claim 2, wherein at least one of said n-CTM compounds is applied in combination with a resin binder to form a charge transporting layer adhering directly to said charge generating layer with one of the two of said layers being itself carried by said electrically conductive support
7. Photosensitive recording material according to claim 6, wherein the resin binder makes that the specific resistivity of the charge transporting layer is not lower than 10^9 ohm.cm.

8. Photosensitive recording material according to claim 6 or 7, wherein the resin binder is a cellulose ester, acrylate or methacrylate resin, polyvinyl chloride, copolyvinyl/acetate and copolyvinyl/maleic anhydride, polyester resins, aromatic polycarbonate resins, polyester carbonate resins, silicone resins, polystyrene, copolymers of styrene and maleic anhydride and copolymers of N-vinylcarbazole having a
5 N-vinylcarbazole content of at least 40 % by weight.
9. Photosensitive recording material according to any of the preceding claims, wherein the content of said n-CTM compound in its layer is 20 to 70 % by weight with respect to the total weight of said layer.
- 10 10. Photosensitive recording material according to claim 1 or 2, wherein the thickness of the layer containing the n-CTM compound(s) is in the range of 5 to 50 μm .

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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 2470

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)
A	EP-A-0 402 980 (AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP) * page 6, line 12 - page 6, line 17; claims * ---	1-10	G03G5/06
A	MONATSHEFTE FÜR CHEMIE vol. 100, no. 2, 12 December 1968, WIEN, AT pages 503 - 509; JUNEK ET AL.: 'Synthesen mit Nitrilen, 23. Mitt.' * Formula 1* ---	1	
D,A	EP-A-0 400 706 (AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP) * claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01 APRIL 1992	Examiner D. Hillebrecht
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			