(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 573 085 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
15.10.1997 Bulletin 1997/42

(51) Int Cl.[6]: **G03G 5/05**

(21) Application number: **93201267.7**

(22) Date of filing: **04.05.1993**

(54) **Photoconductive recording material with moisture-hardened binder system**

Photoleitfähiges Aufzeichnungsmaterial mit feuchtigkeitshärtendem Bindemittelsystem

Matériau d'enregistrement photoconducteur ayant un système de liant durcissable sous l'influence de l'humidité

(84) Designated Contracting States:
BE DE FR GB NL

(30) Priority: **04.06.1992 EP 92201617**

(43) Date of publication of application:
08.12.1993 Bulletin 1993/49

(73) Proprietor: **AGFA-GEVAERT naamloze vennootschap**
2640 Mortsel (BE)

(72) Inventors:
- **Terrell, David, c/o Agfa-Gevaert N.V.**
  B-2640 Mortsel (BE)
- **De Meutter, Stefaan, c/o Agfa-Gevaert N.V.**
  B-2640 Mortsel (BE)
- **Blum, Harald, c/o Agfa-Gevaert N.V.**
  B-2640 Mortsel (BE)

(56) References cited:
EP-A- 0 284 953
EP-A- 0 346 669
US-A- 4 562 132

- **PATENT ABSTRACTS OF JAPAN vol. 11, no. 116 (P-566)(2563) 11 April 1987 & JP - A - 61 262 743.**
- **DATABASE WPIL Section Ch, Week 3386, Derwent Publications Ltd., London, GB; Class A12, AN 86-216879(33) & JP - A - 61 149 963.**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 573 085 B1

Description

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 materials are used to form a latent electrostatic charge image that is developable with finely divided colouring material, called toner.

The developed image can then be permanently affixed to the photoconductive recording material, e.g. a photoconductive zinc oxide-binder layer, or transferred from the photoconductor layer, e.g. a selenium or selenium alloy layer, onto a receptor material, e.g. plain paper and fixed thereon. In electrophotographic copying and printing systems with toner transfer to a receptor material the photoconductive recording material is reusable. In order to permit rapid multiple printing or copying, a photoconductor layer has to be used that rapidly loses its charge on photo-exposure and also rapidly regains its insulating state after the exposure to receive again a sufficiently high electrostatic charge for a next image formation. The failure of a material to return completely to its relatively insulating state prior to succeeding charging/imaging steps is commonly known in the art as "fatigue".

The fatigue phenomenon has been used as a guide in the selection of commercially useful photoconductive materials, since the fatigue of the photoconductive layer limits the copying rates achievable.

A further important property which determines the suitability of a particular photoconductive material for electrophotographic copying is its photosensitivity, which must be sufficiently high for use in copying apparatuses operating with the fairly low intensity light reflected from the original. Commercial usefulness also requires that the photoconductive layer has a spectral sensitivity that matches the spectral intensity distribution of the light source e.g. a laser or a lamp. This enables, in the case of a white light source, all the colours to be reproduced in balance.

Known photoconductive recording materials exist in different configurations with one or more "active" layers coated on a conducting substrate and include optionally an outermost protective layer. By "active" layer is meant a layer that plays a role in the formation of the electrostatic charge image. Such a layer may be the layer responsible for charge carrier generation, charge carrier transport or both. Such layers may have a homogeneous structure or heterogeneous structure.

Examples of active layers in said photoconductive recording material having a homogeneous structure are layers made of vacuum-deposited photoconductive selenium, doped silicon, selenium alloys and homogeneous photoconducting polymer coatings, e.g. of poly(N-vinylcarbazole) or polymeric binder(s) molecularly doped with an electron (negative charge carrier) transporting compound or a hole (positive charge carrier) transporting compound such as particular hydrazones, amines and heteroaromatic compounds sensitized by a dissolved dye, so that in said layers both charge carrier generation and charge carrier transport take place.

Examples of active layers in said photoconductive recording material having a heterogeneous structure are layers of one or more photosensitive organic or inorganic charge generating pigment particles dispersed in a polymer binder or polymer binder mixture in the presence optionally of (a) molecularly dispersed charge transport compound(s), so that the recording layer may exhibit only charge carrier generation properties or both charge carrier generation and charge transport properties.

According to an embodiment that may offer photoconductive recording materials with particularly low fatigue a charge generating and charge transporting layers are combined in contiguous relationship. Layers which serve only for the charge transport of charge generated in an adjacent charge generating layer are e.g. plasma-deposited inorganic layers, photoconducting polymer layers, e.g. on the basis of poly(N-vinylcarbazole) or layers made of low molecular weight organic charge transporting compounds molecularly distributed in a polymer binder or binder mixture.

Useful charge carrier generating pigment materials (CGM's) belong to one of the following classes :

a) perylimides, e.g. C.I. 71130 (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;

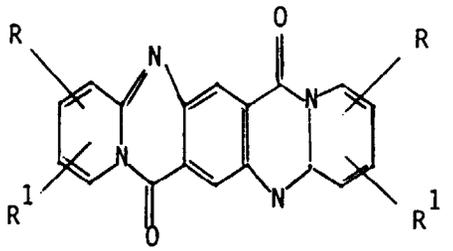
c) quinacridones, e.g. C.I. 46 500 described in DBP 2 237 679;

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;

e) tetrabenzoporphyrins and tetranaphthaloporphyrins, e.g. H_2-phthalocyanine in X-crystal form (X-H_2Pc) described in US-P 3,357,989, 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 tetrabenzoporphyrins described in EP 428.214A; and naphthalocyanines having siloxy groups bonded to the central metal silicon described in published EP-A 243,205;

f) indigo- and thioindigo dyes, e.g. Pigment Red 88, C.I. 73 312 described in DBP 2 237 680;

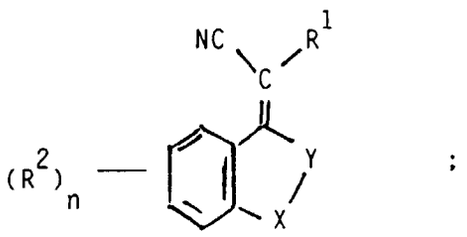
g) benzothioxanthene derivatives as described e.g. in Deutsches Auslegungsschrift (DAS) 2 355 075;
h) perylene 3,4,9,10-tetracarboxylic acid derived pigments including condensation products with o-diamines as described e.g. in DAS 2 314 051;
i) polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, e.g. Chlordiane Blue C.I. 21 180 described in DAS 2 635 887, trisazo-pigments, e.g. as described in US-P 4,990 421 and bisazo-pigments described in Deutsches Offenlegungsschrift (DOS) 2 919 791, DOS 3 026 653 and DOS 3 032 117;
j) squarylium 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 :



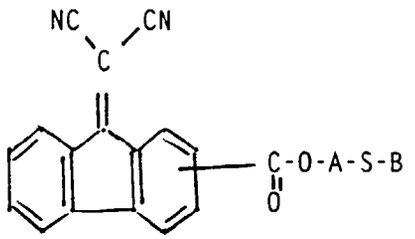
in which R and R^1 are either identical or different and denote hydrogen, C_1-C_4 alkyl, alkoxy, halogen, nitro or hydroxyl or together denote a fuxed aromatic ring system;
m) triarylmethane dyes; and
n) dyes containing 1,5-diamino-anthraquinone groups,
o) inorganic photoconducting pigments e.g. Se, Se alloys, As_2Se_3, TiO_2, ZnO, CdS, etc.

Organic charge carrier transporting substances may be either polymeric or non-polymeric materials.
Preferred non-polymeric materials for negative charge transport are :

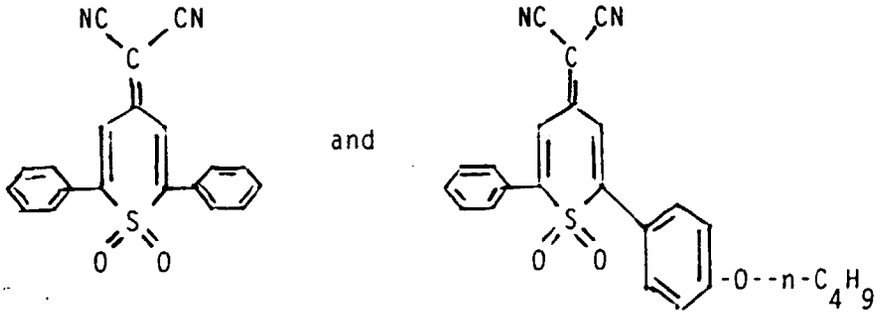
a) dicyanomethylene and cyano-alkoxycarbonylmethylene condensates with aromatic ketones such as 9-dicyanomethylene-2,4,7-trinitrofluorenone (DTF); 1-dicyanomethylene-indan-1-ones as described in published EP application 0 537 808 according to the general formula :



wherein : R^1, R^2, X and Y are as defined in said EP application. or compounds according to the following general formula :



wherein : A is a spacer linkage selected from the group consisting of an alkylene group including a substituted alkylene group, a bivalent aromatic group including a substituted bivalent aromatic group; S is sulfur, and B is selected from the group consisting of an alkyl group including a substituted alkyl group, and an aryl group including a substituted aryl group as disclosed in US-P 4,546,059;
and 4-dicyanomethylene 1,1-dioxo-thiopyran-4-one derivatives as disclosed in US-P 4,514,481 and US-P 4,968,813, e.g.



b) derivatives of malononitrile dimers as described in EP 534,004 A;
c) nitrated fluorenones such as 2,4,7-trinitrofluorenone and 2,4,5,7-tetranitrofluorenone;
d) substituted 9-dicyano methylene fluorene compounds as disclosed in US-P 4,562,132;
e) 1,1,2-tricyanoethylene derivatives.

The choice of binder for the charge generating layer (CGL) for a given charge generating pigment material (CGM) and a charge transport layer (CTL) containing a given charge transport material (CGM) has a strong influence on the electro-optical properties of the photoreceptors. One or more of the following phenomena can have a negative influence on the electro-optical properties of the photoconductive recording material :

1) interfacial mixing between the CGL and the CTL resulting in CGM-doping of the CTL and CTM-doping of the CGL causing charge trapping;
ii) charge trapping in the CGL;
iii) poor charge transport in the CGL;
iv) poor charge transport blocking properties in the absence of a blocking layer.

Interfacial mixing between the CGL and the CTL can be avoided by using a CGL-binder or binders, which is/are insoluble in the solvent used for dissolving the CTL-binders in which CTM's exhibit optimum charge transport properties.

The range of solvents in which both CTL-binders and CTM's are soluble is extremely narrow and often limited to chlorohydrocarbons such as methylene chloride. Methylene chloride is an extremely powerful solvent and the range of CGL-binders which is totally insoluble in methylene chloride is extremely limited, unless the CGL-binder is insolubilized (by crosslinking of polymer chains) in a subsequent hardening process.

Hardening is considered here as a treatment which renders the binder of a charge generating layer of the photoconductive recording material insoluble in methylene chloride.

Various hardenable binder systems have been proposed for CGL's for use with electron-transporting CTL's, for example : polyhydroxy compounds or resins hardened with polyisocyanates, polyepoxy compounds or resins hardened with poly NH-group containing compounds or resins and polyepoxy compounds or resins hardened with polyaminoamides. The hardeners used acting as crosslinking agents, are either highly toxic, induce dermatitis and are subject to moisture induced degradation, or undergo colouration and loss of activity due to oxidation as is the case of poly NH-group containing compounds or resins and polyaminoamides. Moreover, the hardenable binder systems often exhibit a limited potlife as a consequence of premature curing, whereby the CGM-binder dispersion becomes increasingly viscous and reproducible coating becomes impossible.

3. Summary of the invention

It is an object of the present invention to provide a multiple layer photoconductive recording material with improved photosensitivity.

It is a further object of the present invention to provide a photoconductive recording material wherein interfacial

mixing of a charge transporting layer with a charge generating layer is avoided during overcoating of the charge generating layer with a solution of the charge transporting layer composition.

It is still a further object of the present invention to provide a said photoconductive recording material wherein the binder system for the charge generating layer allows efficient charge transport in the charge generating layer and efficient charge injection into the charge transporting layer which is a negative charge transporting layer.

It is another object of the present invention to provide a photoconductive recording material including a charge generating layer the binder of which is cured without need of very toxic components and having after curing good resistance to moisture and oxygen.

Other objects and advantages of the invention will become clear from the following description and examples.

In accordance with the present invention a photoconductive recording material is provided containing a support and a charge generating layer (CGL) in contiguous relationship (contact) with a charge transporting layer (CTL) containing a n-charge transporting material (n-CTM), wherein the binder of said charge generating layer (CGL) is made insoluble in methylene chloride by crosslinking, and said binder is composed essentially of a binder composition hardened under the influence of moisture and prepared by mixing the following components (A) and (B) :

(A) 30 to 99 parts by weight of at least one copolymer of olefinically unsaturated compounds having a weight-average molecular weight [$\overline{M}w$] of at least 1500 and containing chemically incorporated moieties capable of undergoing an addition reaction with amino groups, and

(B) 1 to 70 parts by weight of organic substances containing blocked amino groups from which substances under the influence of moisture compounds having free primary and/or secondary amino groups are formed, and

wherein i) the copolymers of component (A) contain intramolecularly bound carboxylic anhydride moieties, with the anhydride equivalent weight of the copolymers being from 393 to 9,800 and ii) the binder composition contains from 0.25 to 10 anhydride moieties for each blocked amino group.

4. Detailed description of the invention

According to a preferred embodiment the photoconductive recording material according to the present invention has a charge generating layer (CGL) containing as the sole binder one or more resins obtained by mixing and moisture-hardening :

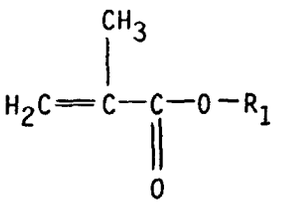
(A) 50 to 97 parts by weight of (a) copolymer(s) of maleic anhydride with at least one other olefinically unsaturated monomer, said copolymer(s) containing addition polymerized maleic anhydride units and having a weight-average molecular weight ($\overline{M}w$) of 1,500 to 75,000, and

(B) 3 to 50 parts by weight of at least one organic substance containing blocked amino groups, said substance having a molecular weight of 86 to 10,000.

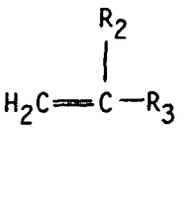
According to a particularly preferred embodiment component (A) consists essentially of a copolymer of :

a) 3 to 25 parts by weight of maleic anhydride, and

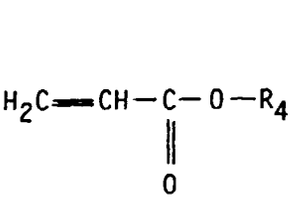
b) 75 to 97 parts by weight of at least one copolymerisable monomer selected from the group corresponding to the following general formulae (I), (II) and (III) :



(I)



(II)



(III)

wherein :

each of R_1 and R_4 independently of each other represents an aliphatic or cycloaliphatic C_1 - C_{18} hydrocarbon group in which one or more carbon atoms may be replaced by heteroatoms selected from the group consisting of

oxygen, sulphur and nitrogen,
R_2 is hydrogen, methyl, ethyl, chlorine or fluorine, and
R_3 is a C_2 - C_{15} aliphatic hydrocarbon group, a C_5 - C_{10} cycloaliphatic hydrocarbon group, a C_7 - C_{18} araliphatic hydrocarbon group, a C_6 - C_{12} aromatic hydrocarbon group containing one or more heteroatoms selected from the group consisting of oxygen, sulphur and nitrogen in the form of ether, ester, amide, urethane, urea, thioester, oxirane, ketone, lactam or lactone group; and

wherein component (B) is a compound selected from the group consisting of an aldimine, ketimine, oxazolane, hexahydropyrimidine, tetrahydroimidazole, dihydroimidazole, tetrahydropyrimidine, amidacetal and amidaminal.

The binder product obtained in curing the above-defined binder composition with the aid of water (moisture) results from the hydrolysis of the blocked amine moieties of component (B), whereby one hydroxyl group is formed per amino group (primary or secondary amino group). These groups, especially said amino groups, enter into rapid cross-linking reaction with the anhydride groups of copolymer (A).

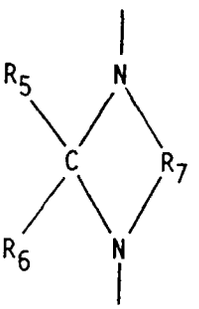
According to a particular embodiment the copolymer containing anhydride groups contains additionally epoxide groups as described in US-P 4,904,740, wherein the last mentioned groups also take part in a crosslinking reaction with free amino groups.

Preferred maleic anhydride copolymers (A) have a weight-average molecular weight [$\bar{M}w$] determined by gel chromatography of 3,000 to 50,000. Their anhydride equivalent weight (= quantity in gram containing 1 mole of anhydride groups) is from 3,800 to 393 and preferably from 2,000 to 450. They are produced in known manner by radically initiated copolymerisation, preferably in the presence of organic solvents. Suitable solvents for that purpose are given in US-P 4,975,493 which also mentions detailed preparation examples of such copolymers. Preferred maleic anhydride copolymers for use according to the present invention contain styrene, methacrylate and/or acrylate units.

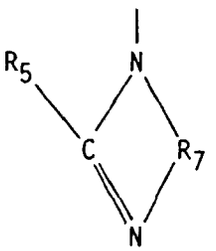
The radical formers applied in the copolymerisation process are those suitable for reaction temperatures of 60 to 180 °C such as organic peroxides and other radical formers mentioned in US-P 4,975,493.

Preferably used blocked amines are oxazolanes, e.g. those described in said US-P 4,975,493. Blocked amines containing aldimine or ketimine groups for generating free amine with water are described in US-P 4,937,293. Blocked amines containing hexahydropyrimidine, tetrahydropyrimidine, or tetrahydroimidazole moieties for generating free amino groups are described in US-P 4,970,270. Blocked amines being amidacetal or amidaminal compounds are described in published European Patent Application 346669.

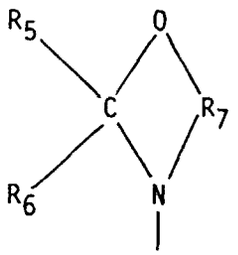
The blocked amines representing said component (B) have preferably a molecular weight of from 86 to 10,000, preferably from 250 to 4,000 and contain a statistical average of from 1 to 50, preferably 1 to 10, especially 2 to 4 structural units corresponding to at least one of the following general formulae (IV), (V), (VI), (VII), (VIII) and (IX):



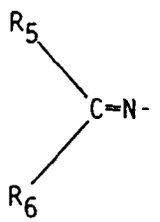
(IV)



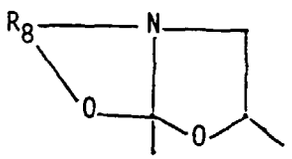
(V)



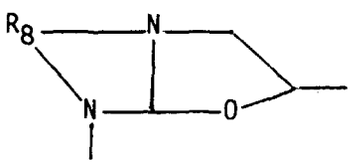
(VI)



(VII)



(VIII)



(IX)

wherein :

each of R_5 and R_6 independently of each other represents hydrogen, an aliphatic hydrocarbon group containing from 1 to 18 carbon atoms, a cycloaliphatic hydrocarbon group containing from 5 to 10 carbon atoms, an araliphatic hydrocarbon group containing from 7 to 18 carbon atoms or a phenyl group, or

R_5 and R_6 represent together the necessary atoms to form a five- or six-membered cycloaliphatic ring with the carbon atom whereto they are commonly linked,

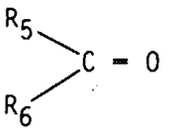
R_7 represents a divalent aliphatic hydrocarbon group containing 2 to 6 carbon atoms, but having only a chain of 2 to 3 carbon atoms between the defined heteroatoms of the ring,

R_8 represents a divalent aliphatic hydrocarbon group having 2 to 10 carbon atoms, but having only 2 or 3 carbon atoms between the heteroatoms whereto said group is linked.

General formula (IV) includes 5-membered tetrahydro-imidazole and 6-membered hexahydropyrimidine structural units. General formula (V) includes 5-membered dihydro-imidazole and 6-membered tetrahydropyrimidine structural units. General formulae (VI), (VII), (VIII) and (IX) relate respectively to oxazolane (VI), aldimine and ketimine (VII), bicyclic amide acetal (VIII) and bicyclic amide aminal (IX) structural units.

Preparation examples of compounds including structural units within the scope of said general formulae are given in US-P 4,975,493 - 4,937,293 - 4,970.270 - and in EP-A-0 346 669.

Suitable aldehydes or ketones for reaction with polyamines to prepare said blocked amines containing hexahydropyrimidine, tetrahydropyrimidine or tetrahydroimidazole units as described above correspond to the following general formula :



wherein R_5 and R_6 have the same meaning as described above, and preferably having a molecular weight of from 72 to 200 for the ketones, and from 58 to 250 for the aldehydes.

The following are examples of these compounds : methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl-n-butyl ketone, methyl-n-amyl ketone, diethyl ketone, cyclohexanone, methyl-tert.-butyl ketone, 3,3,5-trimethyl-cyclohexanone, isobutyraldehyde, 2,2-dimethylpropanal, 2-ethylhexanal, hexanal, octanal, hexahydrobenzaldehyde.

The polyamines used for the preparation of the compounds containing hexahydropyridine or tetrahydroimidazole groups are in particular organic compounds containing at least 2 primary and/or secondary amino groups.

Suitable polyamines are, e.g. those corresponding to the following general formula :

$$R_8 - NH - R_7 - NH - R_9$$

in which

R_7 has the meaning indicated above, and

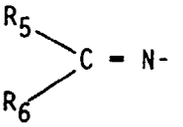
each of R_8 and R_9 (same or different) denote hydrogen, aliphatic hydrocarbon groups containing 1 to 10, preferably 1 to 4 carbon atoms, cycloaliphatic hydrocarbon groups containing 5 to 10, preferably 6 carbon atoms or aromatic hydrocarbon groups containing 7 to 15, preferably 7 carbon atoms, and the above-mentioned hydrocarbon groups, in particular the aliphatic hydrocarbon groups, may contain heteroatoms such as oxygen, nitrogen or sulphur in the form of ether, ester, amide, urethane, oxirane, ketone, lactam, urea, thioether, thioester or lactone groups, and may also contain reactive hydroxyl or amino groups.

Particularly preferred polyamines are those in which R_8 and R_9 (identical or different) stand for an alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, n-pentyl or n-hexyl and at least one of the groups denoted by R_8 and R_9 is a group obtainable by the addition of an amine hydrogen atom to an olefinically unsaturated compound. Examples of olefinically unsaturated compounds suitable for the preparation of such modified polyamines include derivatives of (methyl)acrylic acid such as the esters, amides or nitriles thereof or, e.g. aromatic vinyl compounds such as styrene, α-methylstyrene or vinyl toluene or, e.g. vinyl esters such as vinyl acetate, vinyl propionate or vinyl butyrate or, for example, vinyl ethers such as ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether or mono- or diesters for fumaric acid, maleic acid or tetrahydrophthalic acid.

R_8 and/or R_9 may also stand for an aminoalkyl or hydroxyalkyl group containing, e.g. 2 to 4 carbon atoms.

Ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, 1,2-and 1,3-butylene diamine and diethylene triamine are particularly useful.

The preferred compounds containing aldimine or ketimine groups include compounds containing structural units of the following general formula (R_5 and R_6 having the meaning defined above) :



These compounds in principle may be prepared from the aldehydes or ketones already mentioned above as examples. Preferred aldehydes and ketones used for this purpose include isobutyraldehyde, 2,2-dimethylpropanal, 2-ethylhexanal, hexahydrobenzaldehyde and especially those ketones which have a boiling point below 170°C and are readily volatile at room temperature, e.g. methyl isobutyl ketone, methyl isopropyl ketone, diethyl ketone, diisobutyl ketone and methyl tert.-butyl ketone.

The polyamines used for the preparation of component B) containing ketimine or aldimine groups may in particular be organic compounds containing at least 2 aliphatically and/or cycloaliphatically bound primary amino groups. Although polyamines containing aromatically bound amino groups may also be used, they are less preferred. The polyamines generally have a molecular weight of from 60 to 500, preferably from 88 to 400, although prepolymers with a relatively high molecular weight containing amino end groups may also be used as polyamine components for the preparation of component B).

Diprimary aliphatic and cycloaliphatic diamines are particularly preferred polyamines, e.g. tetramethylene diamine, hexamethylene diamine, isophorone diamine, bis(4-amino-cyclohexyl)-methane, bis-aminomethylhexahydro-4,7-methanoindane, 1,4-cyclohexanediamine, 1,3-cyclohexane diamine, 2-methylcyclohexane diamine, 4-methylcyclohexane diamine, 2,2,5-trimethylhexane diamine, 2,2,4-trimethylhexane diamine, 1,4-butane diol-bis(3-aminopropyl)-ether, 2,5-diamine-2,5-dimethylhexane, bis-aminomethylcyclohexane, bis(4-amino-3,5-dimethylcyclohexyl)-methane and mixtures thereof.

Tetramethylene diamine, hexamethylene diamine, isophorone diamine, bis-aminomethyl-cyclohexane, 1,4-cyclohexane diamine, bis-aminomethylhexahydro-4,7-methanoindane and bis(4-amino-cyclohexyl)-methane are particularly preferred.

The aldimines and ketimines may be prepared not only from these preferred diamines but also from prepolymers containing primary amino end groups, i.e. compounds in the molecular weight range of from 500 to 5,000, preferably from 500 to 2,000, containing at least two amino end groups. These groups include, e.g. the amino polyethers known from polyurethane chemistry, such as these described, e.g. in EP-A-0-081701 or, e.g. compounds containing amide, urea, urethane or secondary amino groups obtained as reaction products of difunctional or higher functional carboxylic acids, isocyanates or epoxides with diamines of the type exemplified above, which reaction products still contain at least two primary amino groups. Mixtures of such relatively high molecular weight polyamines with the low molecular weight polyamines exemplified above may also be used.

The aromatic polyamines which in principle may be used for the preparation of the aldimines or ketimines but are less preferred include, e.g. 2,4- and 2,6-diaminotoluene, 1,4-diaminobenzene and 4,4'-diaminodiphenylmethane.

The compound (B) containing bicyclic amide acetal groups can be obtained in a manner known per se by reaction of compounds containing epoxy or cyclic carbonate groups with cyclic amino esters such as, for example, oxazolines or oxazines. Preferably, the starting components in this reaction are used in such relative amounts that a total of 1.0 to 1.1 oxazoline or oxazine groups is present for every epoxy or cyclic carbonate group. This type of reactions, which lead to compounds having bicyclic amide acetal groups, are described in detail, e.g. in R.Feinauer, Liebigs Ann. Chem. 698, 174 (1966).

The oxazolines or oxazines which are used for the preparation of the bicyclic amide acetals can be prepared by methods known from the literature, e.g. by reaction of carboxylic acids or anhydrides thereof with hydroxyamines with the elimination of water or by reaction of nitriles with hydroxyamines with the elimination of ammonia. This type of reactions is described, e.g. in J. Org. Chem. 26, 3821 (1961), H.L. Wehrmeister, J. Org. Chem. 27, 4418 (1962) and P. Allen, J. Org. Chem. 28, 2759 (1963).

Oxazolines or oxazines which contain hydroxyl groups can also be converted into higher-functional oxazolines or oxazines, e.g. by reaction with organic polyisocyantes.

Bicyclic amide aminals which are suitable according to the invention as component B) can be obtained, e.g. by reaction of tetrahydropyrimidines or dihydroimidazoles with organic epoxides or cyclic carbonates.

In this reaction, monofunctional tetrahydropyrimidines or dihydroimidazoles can be reacted with monofunctional

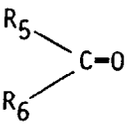
epoxides or carbonates, polyfunctional tetrahydropyrimidines or dihydroimidazoles with monofunctional epoxides or carbonates, monofunctional tetrahydropyrimidines or dihydroimidazoles with polyfunctional epoxides or carbonates.

The tetrahydropyrimidines or dihydroimidazoles used for the preparation of the bicyclic amide aminals can be prepared by methods known from the literature, e.g. by reaction of carboxylic acids with diamines with the elimination of water, or by reaction of nitriles with diamines with the elimination of ammonia. This type of reaction is described, e. g. in DE-OS (German Offenlegungsschrift) 3 640 239.

For the preparation of polymeric dihydroimidazole compounds reference is made to GB-P 1,221,131.

Compounds containing oxazolane groups of the general formula (VI) are especially preferred as component B). They are preferably compounds in which R_5 and R_6, which may be identical or different, denote hydrogen, aliphatic hydrocarbon groups containing from 1 to 18 carbon atoms, cycloaliphatic hydrocarbon groups containing from 5 to 10 carbon atoms, araliphatic hydrocarbon groups containing from 7 to 18 carbon atoms or phenyl groups, or the two groups R_5 and R_6 together with the adjacent carbon atom may form a five- six-membered cycloaliphatic ring, and R_7 denotes a divalent aliphatic hydrocarbon group containing 2 to 6 carbon atoms, with the proviso that there are 2 or 3 carbon atoms between both nitrogen atoms.

Components B) containing oxazolane groups may be prepared in known manner by reaction of the corresponding aldehydes or ketones corresponding to the following general formula (R_5 and R_6 having the meaning defined above) :



with suitable hydroxylamines of the type described hereinafter.

The aldehydes or ketones used may be selected from those already mentioned above as examples. Preferred aldehydes and ketones include isobutyraldehyde, 2-ethylhexanal, hexahydrobenzaldehyde, cyclopentanone, cyclohexanone, methylcyclohexanone, acetone, methyl ethyl ketone and methyl isobutyl ketone.

The hydroxylamines may be in particular organic compounds containing at least 1 aliphatic amino group and at least 1 aliphatically bound hydroxyl group. Although hydroxylamines containing aromatically or cycloaliphatically bound amino or hydroxyl groups may be used, they are less preferred. The hydroxylamines generally have a molecular weight of from 61 to 500, preferably from 61 to 300.

The following are examples of suitable hydroxylamines : bis(2-hydroxyethyl)-amine, bis(2-hydroxypropyl)-amine, bis(2-hydroxybutyl)-amine, bis(3-hydroxypropyl)-amine, bis(3-hydroxyhexyl)-amine, N-(2-hydroxypropyl)-N-(2-hydroxyethyl)-amine, 2-(methylamino)-ethanol, 2-(ethylamino)-ethanol, 2-(propylamino)-ethanol, 2-(butylamino)-ethanol, 2-(hexylamino)-ethanol, 2-(cyclohexylamino)-ethanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1-propanol, 2-amino-2-propyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-3-methyl-3-hydroxybutane, propanolamine and ethanolamine.

The following are particularly preferred : bis(2-hydroxy-ethyl)-amine, bis(2-hydroxypropyl)-amine, bis(2-hydroxybutyl)-amine, bis(3-hydroxyhexyl)-amine, 2-(methylamino)-ethanol, 2-(ethylamino)-ethanol, 2-amino-2-methyl-1-propanol, 2-amino-2-ethyl-1-propanol, propanolamine and ethanolamine.

When component (B) contains oxazolane groups it can be prepared by allowing to react the above-defined reactants in such quantitative ratios that based on the carbonyl groups of the aldehydes or ketones, the hydroxyamines are present in 1 to 1.5 times the equivalent quantity in the oxazolane formation. Catalytic quantities of acidic substances, e.g. p-toluene sulphonic acid, hydrogen chloride, sulphuric acid or aluminium chloride, may be used to accelerate the reaction. A suitable reaction temperature is in the range of 60 to 180 °C, the water formed in the reaction being removed by distillation using an entraining agent as described in US-P 4,975,493.

To produce components (B) having in their molecule a plurality of oxazolane moieties, mono-oxazolanes according to the above mentioned general formula (V) are allowed to react through hydrogen on their nitrogen atom with a polyfunctional reactant, e.g. polyisocyanate, polyepoxide, polycarboxylic acid, partially esterified polycarboxylic acid or polyacid anhydride. The reaction with organic polyisocyanates is preferred and may be carried out as described in DE-OS 2 446 438.

Examples of polyisocyanates which are suitable for this modifying reaction are aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanates, such as those described, e.g. by W. Siefken in Justus Liebigs Annalen de Chemie, 562, p. 75 to 136, e.g. 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane 1,3-diisocyanate, cyclohexane 1,3-diisocyanate, cyclohexane 1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 1,4- and 2,6-hexahydrotoluylene diisocyanate, hexahydrol-1,3- and -1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene disocyanate, diphenylmethane-2,4'-

and/or 4,4'-diisocyanate, naphthylene 1,5-diisocyanate, mixtures of these and other polyisocyanates, polyisocyanates having carbodiimide groups (as described e.g. in German Patent Specification 1 092 007), polyisocyanates having allophanate groups (as described e.g. in GB-P 994,890), polyisocyanates having isocyanurate groups (as described e.g.in in German Patent Specifications 1 022 789 and 1 222 067) polyisocyanates having urethane groups (as described e.g. in US-P 3,394,164) or polyisocyanates prepared by reaction of at least one difunctional hydroxyl compound with excess of at least one difunctional isocyanate, polyisocyanates having biuret groups (as described e.g. in German Patent Specification 1 101 394) and prepolymer or polymer substances having at least two isocyanate groups.

Examples of suitable polyisocyanate compounds are further given in the book High Polymers, Volume XVI dealing with "Polyurethanes, Chemistry and Technology" Interscience Publishers, New York, London, and further also in Volume I, 1962, p. 32-42 and 45-54 and Volume II, 1964, p. 5-6 and 198-199, and also in Kunststoffhandbuch (Handbook of Plastics), Volume VI, Vieweg-Höchtlen, Carl-Hanser Verlag, Munich, 1966, p. 45-71.

Particularly preferred polyisocyanates for preparing polyfunctional oxazolanes are low molecular weight (cyclo) aliphatic diisocyanates, e.g. : hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-diisocyanatodicyclohexyl-methane or relatively high molecular weight isocyanate prepolymers based on such diisocyanates.

According to a preferred embodiment in the formation of polyfunctional oxazolanes said preferred polyisocyanates are allowed to react with monooxazolanes according to the above-mentioned general formula (VI) wherein nitrogen is linked to a $HO\text{-}CH_2\text{-}CH_2$- group to form an urethane linkage, R_5 represents hydrogen, R_6 an ethyl-1-pentyl group, and R_7 is an ethylene group.

Polyepoxides suitable for use in the preparation of polyfunctional oxazolanes are organic compounds containing at least two epoxide groups.

Preferred polyepoxides for such use are aliphatic bisepoxides having epoxide equivalent weights of 43 to 300, e. g. 1,3-butadiene bisepoxide, 1,5-hexadiene bisepoxide, ethylene glycol diglycidyl ether, glycerol-1,3-diglycidyl ether, 3,4-epoxycyclohexyl, methyl-3',4'-epoxycyclohexane carboxylate, and adipic acid-(3,4-epoxycyclohexyl)-bisester.

Still other methods of preparing oxazolanes of relatively high functionality are described in the already mentioned US-P 4,975,493.

The molecular weight and functionality of the oxazolanes of relatively high functionality may be adjusted readily through the choice of the reactants.

For use according to the present invention in the preparation of a moisture-curable binder for charge generating material particles of a charge generating layer of a photoconductive recording material, di- and/or trifunctional oxazolanes are applied preferably in conjunction with a copolymer of maleic anhydride and other monomers, e.g. styrene, methyl methacrylate and butyl acrylate, containing at least 10 % by weight of polymerised maleic anhydride units.

The following illustrates in detail the preparation of specific components (A) and (B) suited for use according to the present invention.

I. Preparation of the maleic anhydride copolymers A

General procedure for preparing the maleic anhydride copolymers A_1-A_9 mentioned in Table 1 under the heading MSA-copolymers A :

Part I is introduced initially into a reaction vessel equipped with a stirring, cooling and heating system, heated to the reaction temperature. Part II is added over a period of 3 hours and part III over a period of 3,5 hours, followed by stirring for 2 hours.

The reaction temperatures and the composition of parts I - III are shown in the following Table 1 together with the solids content and viscosity of the maleic anhydride (MA) copolymer solutions obtained.

TABLE 1

MA-Copolymers A (Quantities in g)

	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
Part I									
Butyl acetate	1050	1534	1400			798	1670		1500
Methoxypropyl acetate				1200	800			1891	
Xylene							3300		
Part II									
Xylene							1400		
Methyl methacrylate	859	780	1025		600	675	1080		120
Styrene	313	180	341	450	30	350	3360	1013	870
Butyl acrylate	300	300	732	675	327.5	1056	4560	563	1410
Glycidyl methacrylate		120							
Maleic anhydride	284	120	244	375	40	425	2400	300	480
Hexanediol bisacrylate					2.5				
Butyl acetate						1275	1000		449
n-Dodecylmercaptan					10				
Part III									
2,2'-azobis(isobutyronitrile)				30	20				
Ditert.butyl peroxide							600		
tert.-butyl peroctoate (70%)	105	86	140			105		233	171
Xylene							600		
Methoxypropyl acetate				330	200				
Butyl acetate	360		118						
Reaction temperature (°C)	115	120	120	130	120	126	150	145	125
Solids content (%)	55.2	50.0	60.4	55.7	40.6	56.4	60.0	49.3	59.5
Viscosity (mPa.s)	11100	900		18700	576	1100	1100		2100
Anhydride equivalent weight (g) (theory) (1 mol MA/1 mol sec. amine)	605	1225	940	392	2450	578	465	613	588

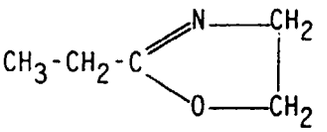
II. Preparation of blocked polyamines B

B 1) The bisketimine B 1 is obtained from 680 g of isophoronediamine, 1000 g of methyl isobutyl ketone and 560

g of toluene after separation of 146 g of water (theoretical quantity : 144 g) at 120°C and subsequent distillation.

B 2) 200 g of isobutyraldehyde and 133 g of cyclohexane are introduced under nitrogen atmosphere into a 1-l reaction vessel equipped with stirring, cooling and heating means and the reaction mixture is cooled to 10°C in an ice bath. Thereupon 176.6 g of 1-amino-3-(methylamino)-propane are slowly added dropwise and the reaction mixture is stirred at 10°C for one hour. It is then heated to reflux temperature until 52 g of water have separated off. After removal of the solvent and unreacted blocking agent by distillation hexahydropyrimidine is obtained.

B 3) By transforming propionic anhydride and aminoethanol by refluxing in xylene under azeotropic elimination of the reaction water (H.L. Wehrmeister, J. Org. Chem., 26, 3821 (1961)) a monooxazoline as defined hereinafter by structural formula is obtained that is purified by distillation :



99 g of this monooxazoline, 88 g of ethylene carbonate and 0.4 g of lithium chloride are heated at 150°C for 12 h. After distillation the colourless, bicyclic amidacetal crosslinking agent B 3) is obtained.

B 4) By transforming 528 g of 1-amino-3-methylaminopropane and 360 g of acetic acid in 99 g of toluene and elimination of the reaction water at 100 to 130°C a tetrahydropyrimidine precursor is obtained (theor. : 216 g; found : 212.5 g), which after distillation is obtained in about 90 % yield as a bright and colourless liquid.
112 g of tetrahydropyrimidine precursor are made to react in 200 g of butyl acetate with 87 g of ethylene glycol diglycidyl ether at 120 to 130°C for 5 h. After adding charcoal the reaction mixture is stirred for still 1 h, and filtered off unter nitrogen atmosphere. A yellow solution (about 50 %) of the difunctional bicyclic amidaminal B 4) is obtained.

Preparation of mono-oxazolanes and poly-oxazolanes B :

General procedure :

To prepare the mono-oxazolanes, the hydroxyamines, the carbonyl compounds and, optionally, the entraining agent are mixed and 0.01 to 0.1 % of an acidic catalyst is added optionally to the resulting mixture. The reaction mixture is then heated under reflux in an inert gas atmosphere (e.g. N_2, Ar) on a water separator until the theoretical quantity of water has separated off or until no more water separates off. The products thus obtained may be used for the combinations according to the invention without any further purification or separation step. When the purity or uniformity of the products has to meet particularly exacting requirements, the products may be purified, e.g. by vacuum distillation.

B 5) The mono-oxazolane B 5) is obtained from 210 g of diethanolamine, 158.4 g of isobutyraldehyde and 92.1 g of xylene after separation of 34.2 g of water (theoretical quantity : 36 g).

B 6) 536 g of trimethylolpropane, 1368 g of ε-caprolactone, 476 g of dimethyldiglycol and 0.4 g of an esterification catalyst (tin dioctoate) are heated together to 140°C for 4 h. Thereupon 297.5 g of the trimethylolpropane/ε-caprolactone adduct thus prepared and 265.0 g of oxazolane B 5) are heated together to 50°C. After the dropwise addition of 252 g of hexamethylene diisocyanate, the mixture is stirred at 70°C for 6 h. The poly-oxazolane B 6) is obtained in the form of a 70% solution after the addition of 113 g of dimethyl diglycol.

B 7) The mono-oxazolane B 7) is obtained by condensation reaction from 210 g of diethanolamine, and 281.6 g of 2-ethylhexanal in 122.9 g of cyclohexane after separation of 35 g of water (theoretical quantity : 36 g).

B 8) 400 g of an aliphatic polyisocyanate containing biuret groups and based on the reaction with water of hexamethylene diisocyanate and 397 g of methoxypropyl acetate are introduced into a 2-litre reaction vessel equipped with stirrer, condenser and heating device. After the dropwise addition of 526.1 g of the oxazolane of diethanolamine and 2-ethylhexanal described in B 7), the temperature of the reaction mixture is maintained at 70°C for 11 h. An approximately 70 % solution of poly-oxazolane agent B 8) containing a statistical average of 3 oxazolane groups

pro macromolecule is obtained, i.e. 1.754 mmol of oxazolane units are contained in 1 g of 70 %wt solution.

B 9)

step a) 296 g of phthalic anhydride, 324 g of cyclohexane dimethanol and 52 g of neopentyl glycol are weighed in a reaction vessel suitable for esterification under a nitrogen atmosphere and heated to 220°C for 8 h. Water is separated until the acid number has reached or dropped below 2.5. The polyester precursor B 9 a) is obtained.

step b) 145.2 g of the polyester precursor obtained in said step a) and 113.4 g of methoxypropyl acetate are weighed into a 1-litre reaction vessel equipped with stirrer, condenser and heating device and heated to 60°C. Thereupon 119.5 g of the mono-oxazolane B 7) obtained from diethanolamine and 2-ethylhexanal is then added dropwise and stirring is continued at 70°C for 3 h. After the addition of 318.4 g of polyester precursor B 9 a), the temperature is maintained at 70°C for 11 h and cross-linking agent B 9) which is a polyester-based poly-oxazolane is then obtained as a 70 % solution.

B 10) poly-oxazolane is prepared from 187.8 g of an isocyanurate polyisocyanate, which has been prepared by partial trimerisation of the NCO groups of hexamethylene diisocyanate in accordance with EP-A-No. 10589 and which has an NCO content of 21.45 % by weight, and 1623 g of oxazolane (obtained as described for B 5) but from 1728 g of methyl ethyl ketone and 2100 g of diethanolamine). The highly viscous product is dissolved in butyl acetate to from a 70 % solution. The solution has a viscosity of 900 mPa.s at 23°C.

B 11) polyoxazolane is prepared from 840 g of hexamethylene diisocyanate and 2360 g of oxazolane B 7). The product has a viscosity of 4000 mPa.s at 23°C.

In the preparation of a preferred binder for use according to the present invention a mixture of components (A) and (B) is made in a water-free organic solvent or solvent mixture and the charge generating material particles are dispersed therein to form a charge generating layer composition ready for coating. The solvent(s) are used in a quantity necessary to obtain the required coating composition viscosity adapted to the applied coating system. The quantity of solvent may be kept fairly small by applying low molecular weight maleic anhydride copolymers.

According to a particular embodiment dispensing with solvent removal after coating, a liquid monomer or mixture of monomers is used that acts as solvent for the applied components (A) and (B). Said monomer or mixture of monomers, which has not to be removed by evaporation, can be polymerised at elevated temperature in the presence of a thermally activatable radical former for addition polymerisation.

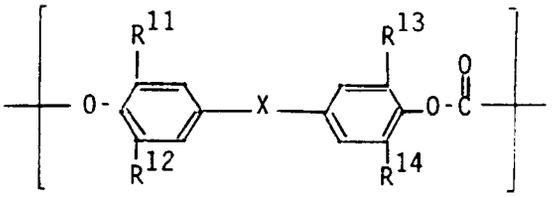
The hardening of the binder obtained by reaction of components (A) and (B) proceeds quickly in the presence of atmospheric moisture entering the coating after its application. The hardening may be accelerated by heat e.g. in the temperature range of 40 to 130 °C, temperature at which applied solvents are removed by evaporation.

The resins obtained by reaction of said components (A) and (B) with moisture may be used in combination with at least one other polymer serving as binding agent, e.g. in combination with acrylate and methacrylate resins, copolyesters of a diol, e.g. glycol, with isophthalic and/or terephthalic acid, polyacetals, polyurethanes, polyester-urethanes, aromatic polycarbonates.

Useful resin combinations contain at least 50 % by weight of said resins obtained by moisture-hardening of a mixture of components (A) and (B) in the total binder content.

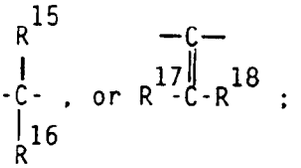
A polyester resin particularly suited for use in combination with said hardened resins is a polyester sold under the tradename DYNAPOL L 206 (DYNAPOL is a registered trade mark of Dynamit Nobel for a copolyester of terephthalic acid and isophthalic acid with ethylene glycol and neopentyl glycol, the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

Aromatic polycarbonates that are suitable for use in admixture with said resins (1) and/or (2) hardened with polyisocyanates are aromatic polycarbonates that 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 (Z):



(Z)

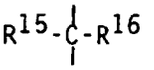
in which : X represents S, SO_2,



each of R^{11}, R^{12}, R^{13}, R^{14}, R^{17} and R^{18} (same or different) represents hydrogen, an alkyl group or an aryl group, and each of R^{15} and R^{16} (same or different) represents hydrogen, an alkyl group, an aryl group or together represent the necessary atoms to close a cycloaliphatic ring, e.g. a cyclohexane ring.

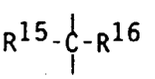
Aromatic polycarbonates having a molecular weight in the range of 10,000 to 200,000 are preferred. Suitable polycarbonates having such a high molecular weight are sold under the registered trade mark MAKROLON of Bayer AG, W-Germany.

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^{11}, R^{12}, R^{13} and R^{14}=H, X is



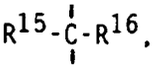
with R^{15}=R^{16}=CH3.

MAKROLON 5700 (registered trade mark) is a bisphenol A polycarbonate with molecular weight in the range of 50,000 to 120,000 wherein R^{11}, R^{12}, R^{13} and R^{14}=H, X is



with R^{15}=R^{16}=CH3.

Bisphenol Z polycarbonate is an aromatic polycarbonate containing recurring units wherein R^{11}, R^{12}, R^{13} and R^{14}=H, X is



and R^{15} together with R^{16} represents the necessary atoms to close a cyclohexane ring.

Suitable electronically inactive binder resins for use in unhardened active layers of the present photoconductive recording material are cellulose esters, acrylate and methacrylate resins, e.g. cyanoacrylate resins, polyvinyl chloride, and copolymers of vinyl chloride, e.g. copolyvinyl chloride/acetate and copolyvinyl chloride/maleic anhydride, polyester resins e.g. copolyesters of isophthalic acid and terephthalic acid with glycol and aromatic polycarbonate resins.

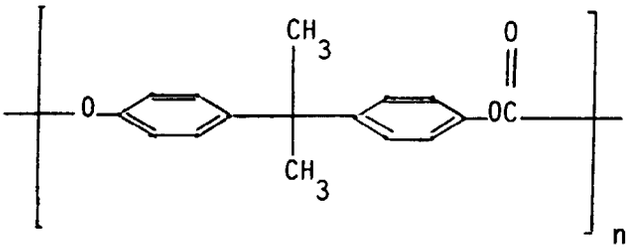
Further useful unhardened binder resins for an active layer are silicone resins, polystyrene and copolymers of styrene and maleic anhydride and copolymers of butadiene and styrene.

A charge transport layer in the photoconductive recording materials of the present invention preferably has a thickness in the range of 5 to 50 µm, more preferably in range of 5 to 30 µm. If such a layer contains low molecular weight charge transport molecules, such compounds will preferably be present in concentrations of 30 to 70 % by

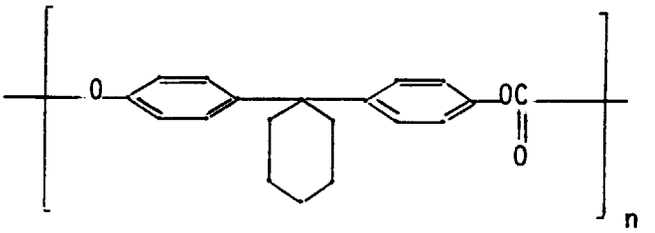
weight.

Preferred binders for a negative charge transporting (CTL) layer in the recording material of the present invention are homo- or co-polycarbonates within the scope of the general formula (Z) above, more particularly specific polycarbonates and copoly-carbonates with recurring units B1 to B7.

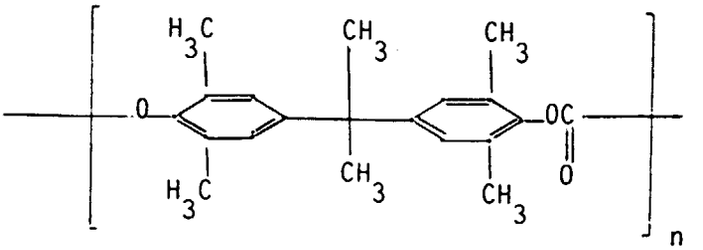
B1



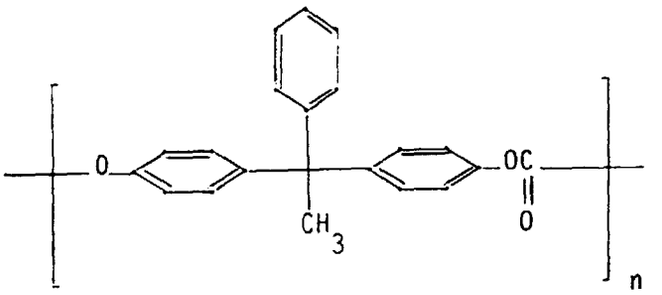
B2

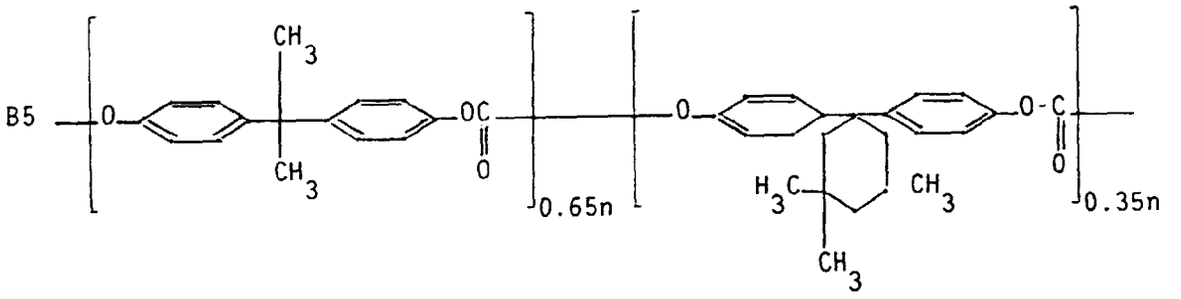


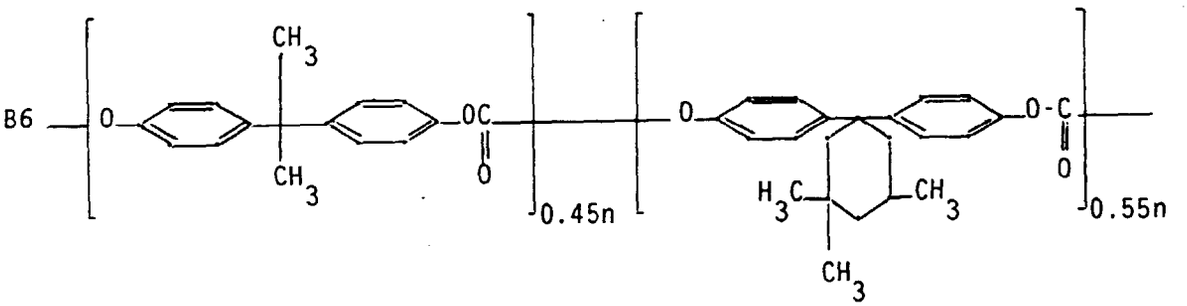
B3



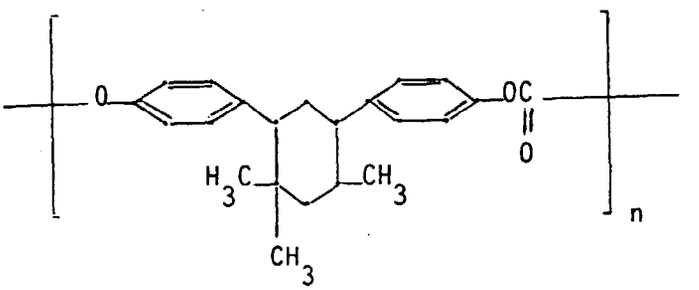
B4







B7



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 underlying charge generating layer still can receive a substantial amount of the exposure light when exposed through the charge transporting layer.

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 derivatives is such that the acceptor/donor weight ratio range is from 2.5:1 to 1,000:1.

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.

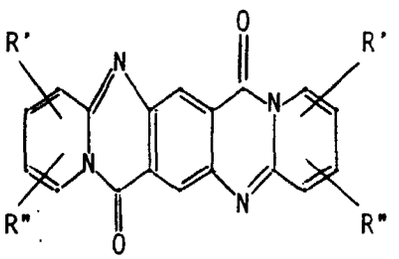
For controlling the viscosity of the coating compositions and controlling their optical clarity silicone oils may be added to the charge transport layer.

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.

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) perylimides, 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,
e) tetrabenzoporphyrins and tetranaphthaloporphyrins, e.g. H_2-phthalocyanine in X-crystal form (X-H_2Pc) described in US-P 3,357,989, metal phthalocyanines, e.g. CuPc C.I. 74 160 described in DBP 2 239 924, indium phthalocyanine described in US-P 4,713,312, tetrabenzoporphyrins described in EP 428,214A, silicon naphthalocyanines having siloxy groups bonded to the central silicon as described in EP-A 0243205 and X- and β-crystal morphology $H_2Pc(CN)_x$, $H_2Pc(CH_3)_x$ and N_2PcCl_x pigments,
f) indigo- and thioindigo dyes, e.g. Pigment Red 88, C.I. 73 312 described in DBP 2 237 680,
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 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 :



wherein R' and R" have the meaning described in GB-P 1,416,602.

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, cadmium-selenide, cadmium sulphide and mixtures thereof as disclosed in US-P 4,140,529.

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 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 aluminium, steel, brass and paper and resin materials incorporating or coated with conductivity enhancing substances.

An insulating support such as a resin support is e.g. provided with a conductive coating, e.g. vacuum-deposited metal such as aluminium, 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 electrostatically charging, charging, e.g. with corona-device, the photoconductive layer containing as binder essentially at least one resin obtained by the reaction in the presence of moisture of said components (A) and (B);

(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 containing on an electrically conductive support a photosensitive charge generating layer that contains as binder essentially at least one resin obtained by the reaction in the presence of moisture of said components (A) and (B), in contiguous relationship with a charge transporting layer, 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.

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 16 different exposures in addition to 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 10 cm/s. The recording material was sequentially charged with a positive corona at a voltage of + 5.7 kV operating with a grid voltage of + 600 V. 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 200 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 355 mJ/m2 positioned at an angle of 270° with respect to the corona source a new copying cycle started. Each measurement relates to 80 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 0.2, 0.38, 0.55, 0.73, 0.92, 1.02, 1.20, 1.45, 1.56, 1.70, 1.95, 2.16, 2.25, 2.51 and 3.21 each for 5 cycles and finally to zero light intensity for the last 5 cycles.

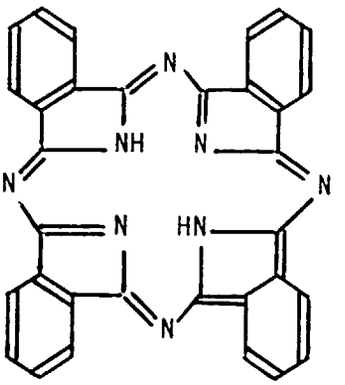
The electro-optical results quoted in the EXAMPLES 1 to .. hereinafter refer to charging level at zero light intensity (CL) and to discharge at a light intensity corresponding to the light source intensity moderated by a grey filter to the exposure indicated to a residual potential RP.

The % discharge is :

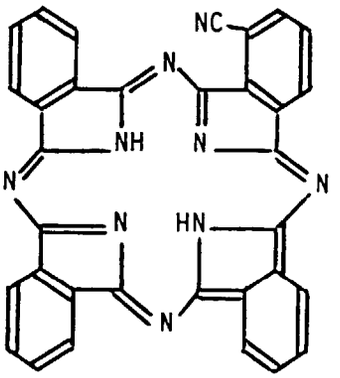
$$\frac{(CL-RP)}{CL} \times 100$$

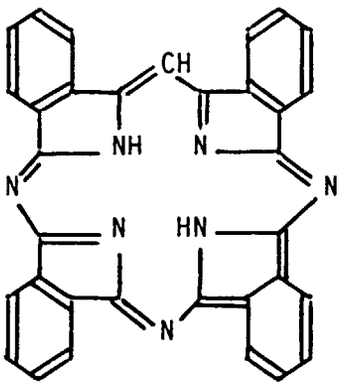
For a given corona voltage, corona grid voltage, separating distance of the corona wires to recording surface and drum circumferential speed the charging level CL is only dependent upon the thickness of the charge transport layer and its specific resistivity. In practice CL expressed in volts should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

Charge generating materials (CGM's) used in the following examples have the following formulae :

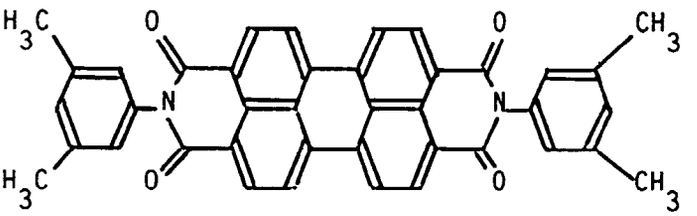
X-H_2Pc  in X-morphology

X-$H_2Pc(CN)_{0.36}$: mixed crystalline pigment consisting of 1.75:1 molar ratio of H_2Pc and

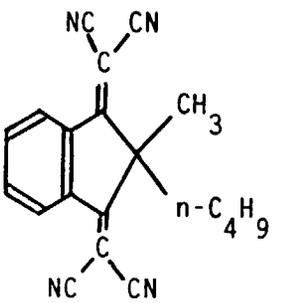
 in X-morphology

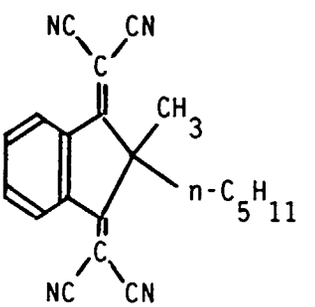
ω-H_2TTP  in ω-morphology

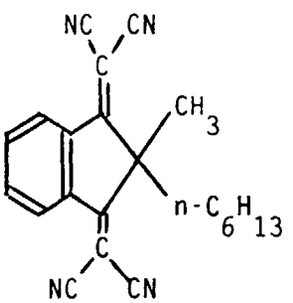
Perylene pigment :

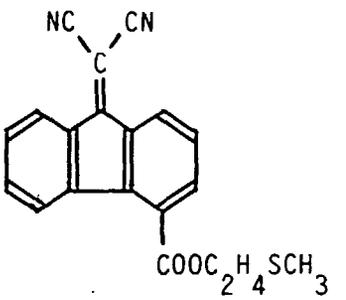


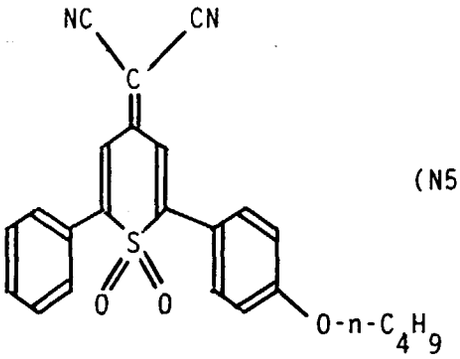
Negative charge transporting compounds (CTM), i.e. electron-transporting compounds, (N1 to N8) used in the following Examples are given hereinafter :

 (N1) ;

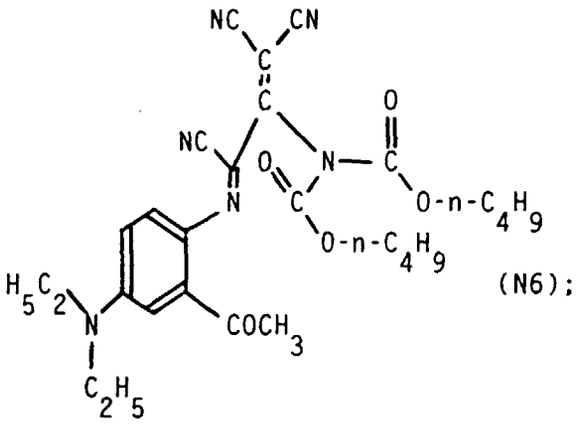
 (N2) ;

 (N3) ;

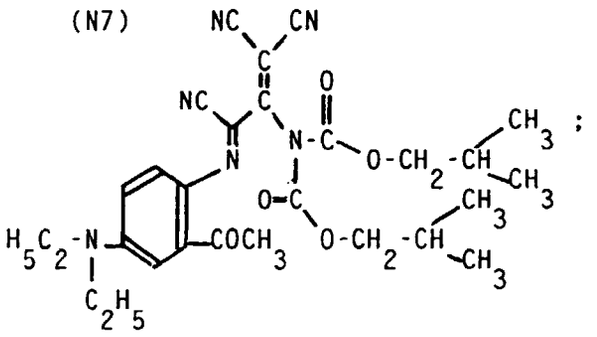
 (N4) ;



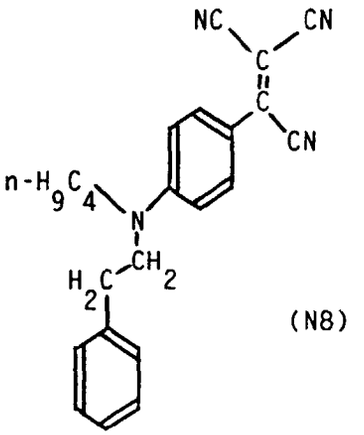
(N5) ;



(N6);



(N7)



(N8)

All parts, ratios and percentages are by weight unless otherwise stated.

EXAMPLE 1

In the production of a composite layer electrophotographic recording material a 175 µm thick polyester film pre-coated with a vacuum-deposited layer of aluminium was doctor-blade coated with a dispersion of charge generating pigment to a thickness of 0.9 µm.

Said dispersion was prepared by mixing 2 g of metal-free X-phthalocyanine (FASTOGEN Blue 8120B from Dainippon Ink and Chemical Inc.); 0.5 g of MA-copolymer A_7 (see Table 1); 9.71 g of butan-2-one and 16.54 g of methylene chloride for 40 hours in a ball mill.

0.7 g of said MA-copolymer A_7, 1 g of poly-oxazolane B 8 [70 % solution in butyl acetate], 8.25 g of methylene chloride and 4.85 g of butan-2-one were then added to the dispersion and mixing continued for a further 15 minutes.

The applied layer was dried and thermally moisture-hardened for 2 hours at 50 °C and the overcoated using a doctor-blade coater with a filtered solution of 2.5 g of the CTM N2; 3.05 g of MAKROLON 5700 (tradename for a bisphenol A-polycarbonate from Bayer AG); and 40.7 g of methylene chloride to a thickness of 11.1 µm after drying at 50 °C for 16 hours.

The electro-optical characteristics of the thus obtained photoconductive recording material were described as defined above.

At a charging level (CL) of +556 V and an exposure with 660 nm light, ($I_{660}t$) of 20 mJ/m^2, the following results were obtained :

CL = +556 V
RP = +118 V
% discharge = 78.8.

EXAMPLES 2 AND 3

The photoconductive recording materials of examples 2 and 3 were produced as described for example 1 except that the amounts of MA-copolymer A_7 and polyoxazolane B 8 and were varied as given in Table 1 together with the CTL layer thicknesses (d_{CTL}).

The electro-optical properties of the thus obtained photoconductive recording materials were determined as described above and the results are summarized in Table 2 together with those for the photoconductive recording material of example 1.

TABLE 2

Example No. discharge	MA-copolymer $A_{7\ [wt\%]}$	Polyoxazolane B 8 [wt%]	d_{CTL}	$I_{660}t$ = 20 mJ/m²		
			[µm]	CL [V]	RP [V]	%
2	12.5	37.5	10.1	622	463	25.6
1	25	25	11.1	556	118	78.8
3	37.5	12.5	12.1	579	188	67.5

EXAMPLES 4 TO 8

The photoconductive recording materials of examples 4 to 8 were produced as described for example 1 except that alternative CTM's were used instead of N2. The CTL layer thicknesses are given in Table 2 together with the CTM concentrations used.

The electro-optical properties of the thus obtained photoconductive recording materials wer determined as described above and the results are summarized in Table 3 together with those for the photoconductive recording material of example 1.

TABLE 3

Example No.	CTM	CTM conc.	d_{CTL}	λ	It = 20 mJ/m²		
		[wt%]	[µm]	[nm]	CL [V]	RP [V]	% discharge
4	N1	45	13.1	780	544	100	81.6
1	N2	45	11.1	660	556	118	78.8
5	N3	45	11.1	780	556	115	79.3
6	N6	50	13.1	780	527	142	73.1
7	N7	50	11.1	780	505	150	70.3
8	N3	50	12.1	780	557	270	51.5

EXAMPLES 9 AND 10

The photoconductive recording materials of examples 9 to 10 were produced as described for example 1 except that different CGM's were used. The CTL layer thicknesses are given in Table 4.

The electro-optical properties of the thus obtained photoconductive recording materials wer determined as described above and the results are summarized in Table 4 together with those for the photoconductive recording material of example 1.

TABLE 4

Example No.	CGM	d_{CTL}	$I_{660}t$ = 20 mJ/m²		
		[µm]	CL [V]	RP [V]	% discharge
1	FASTOGEN BLUE 8120B	13.1	556	118	78.8
9	X-$H_2Pc(CN)_{0.36}$	11.1	527	125	76.3
10	ω-H_2TTP	10.1	552	236	57.2

Claims

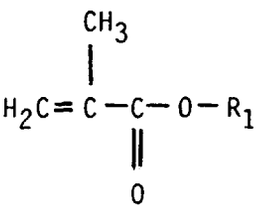
1. A photoconductive recording material containing a support and a charge generating layer (CGL) in contiguous relationship with a charge transporting layer (CTL) containing a n-charge transporting material (n-CTM), wherein the binder of said charge generating layer (CGL) is made insoluble in methylene chloride by crosslinking, and said binder is composed essentially of a binder composition hardened under the influence of moisture and prepared by mixing the following components (A) and (B) :

   (A) 30 to 99 parts by weight of at least one copolymer of olefinically unsaturated compounds having a weight-average molecular weight [$\overline{M}w$] of at least 1500 and containing chemically incorporated moieties capable of undergoing an addition reaction with amino groups, and
   (B) 1 to 70 parts by weight of organic substances containing blocked amino groups from which substances under the influence of moisture compounds having free primary and/or secondary amino groups are formed, and

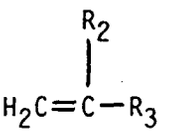
   wherein i) the copolymers of component (A) contain intramolecularly bound carboxylic anhydride moieties, with the anhydride equivalent weight of the copolymers being from 393 to 9,800 and ii) the binder composition contains from 0.25 to 10 anhydride moieties for each blocked amino group.

2. Photoconductive recording material according to claim 1, wherein said component (A) consists essentially of a copolymer of :

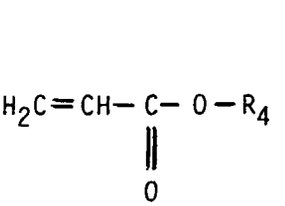
   a) 3 to 25 parts by weight of maleic anhydride, and
   b) 75 to 97 parts by weight of at least one copolymerisable monomer selected from the group corresponding to the following general formulae (I), (II) and (III) :



(I)



(II)



(III)

   wherein :

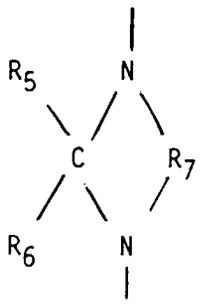
   each of R_1 and R_4 independently of each other represents an aliphatic or cycloaliphatic C_1 - C_{18} hydrocarbon group in which one or more carbon atoms may be replaced by heteroatoms selected from the group consisting of oxygen, sulphur and nitrogen,
   R_2 is hydrogen, methyl, ethyl, chlorine or fluorine, and
   R_3 is a C_2 - C_{15} aliphatic hydrocarbon group, a C_5 - C_{10} cycloaliphatic hydrocarbon group, a C_7 - C_{18} araliphatic hydrocarbon group, a C_6 - C_{12} aromatic hydrocarbon group containing one or more heteroatoms selected from the group consisting of oxygen, sulphur and nitrogen in the form of ether, ester, amide, urethane, urea, thioester, oxirane, ketone, lactam or lactone group; and

   wherein component (B) is a compound selected from the group consisting of an aldimine, ketimine, oxazolane, hexahydropyrimidine, tetrahydroimidazole, dihydroimidazole, tetrahydropyrimidine, amidacetal and amidaminal.

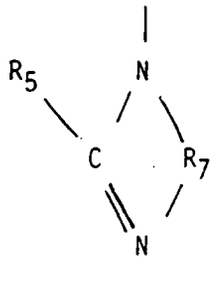
3. Photoconductive recording material according to claim 2, wherein said maleic anhydride copolymers (A) have a weight-average molecular weight [Mw] determined by gel chromatography of 3,000 to 50,000, and their anhydride equivalent weight (= quantity in gram containing 1 mole of anhydride groups) is from 3,800 to 393.

4. Photoconductive recording material according to claim 2, wherein said maleic anhydride copolymers (A) contain styrene, methacrylate and/or acrylate units.

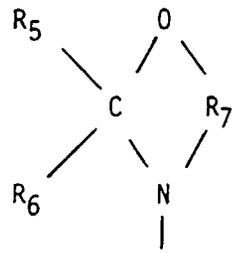
5. Photoconductive recording material according to claim 1, wherein component (B) contains a statistical average of from 1 to 50 structural units corresponding to at least one of the following general formulae (IV), (V), (VI), (VII), (VIII) and (IX):



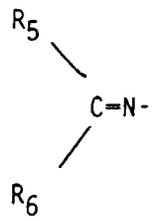
(IV)



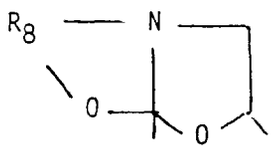
(V)



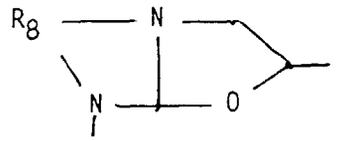
(VI)



(VII)



(VIII)



(IX)

wherein :

each of R_5 and R_6 independently of each other represents hydrogen, an aliphatic hydrocarbon group containing from 1 to 18 carbon atoms, a cycloaliphatic hydrocarbon group containing from 5 to 10 carbon atoms, an araliphatic hydrocarbon group containing from 7 to 18 carbon atoms or a phenyl group, or
R_5 and R_6 represent together the necessary atoms to form a five- or six-membered cycloaliphatic ring with the carbon atom whereto they are commonly linked,
R_7 represents a divalent aliphatic hydrocarbon group containing 2 to 6 carbon atoms, but having only a chain of 2 to 3 carbon atoms between the defined heteroatoms of the ring,
R_8 represents a divalent aliphatic hydrocarbon group having 2 to 10 carbon atoms, but having only 2 or 3 carbon atoms between the heteroatoms whereto said group is linked.

6. Photoconductive recording material according to claim 5, wherein component (B) is a polyoxazolane obtained by allowing a mono-oxazolane according to said general formula (V) through hydrogen on its nitrogen atom to react with a polyfunctional reactant selected from the group consisting of a polyisocyanate, polyepoxide, polycarboxylic acid, partially esterified polycarboxylic acid or polyacid anhydride.

7. Photoconductive recording material according to claim 1, wherein said charge generating layer contains as the sole binder one or more resins obtained by moisture-hardening reaction of said mixed components (A) and (B).

8. Photoconductive recording material according to claim 1, wherein said resins obtained by moisture-hardening reaction of said mixed components (A) and (B) are present in combination with at least one other polymer serving as binding agent.

9. Photoconductive recording material according to claim 8, wherein said other polymer is selected from the group consisting of an acrylate resin, methacrylate resin, copolyester of a diol with isophthalic and/or terephthalic acid, polyacetal, polyurethane, polyester-urethane and aromatic polycarbonate.

10. Photoconductive recording material according to claim 1, wherein said support consists of aluminium or is a support provided with an aluminium layer forming a conductive coating.

Patentansprüche

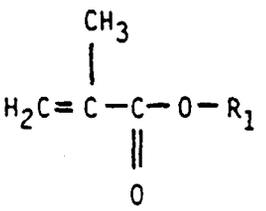
1. Ein fotoleitendes Aufzeichnungsmaterial mit einem Träger und einer ladungserzeugenden Schicht (CGL), die an eine ein Negativladungstransportmaterial (n-CTM) enthaltende Ladungstransportschicht (CTL) grenzt, wobei das Bindemittel der ladungserzeugenden Schicht (CGL) durch Vernetzung unlöslich in Methylenchlorid gemacht ist und wesentlich aus einer durch Feuchtigkeit gehärteten und durch Vermischen der nachstehenden Bestandteile (A) und (B) hergestellten Bindemittelzusammensetzung besteht :

   (A) 30 bis 99 Gewichtsteile von wenigstens einem Copolymeren aus olefinisch ungesättigten Verbindungen, das ein gewichtsdurchschnittliches Molekulargewicht [$\overline{M}w$] von mindestens 1.500 aufweist und chemisch einverleibte Anteile enthält, die zu einer Additionsreaktion mit Aminogruppen befähigt sind, und
   (B) 1 bis 70 Gewichtsteile von blockierte Aminogruppen enthaltenden organischen Substanzen, aus denen sich unter dem Einfluß von Feuchtigkeit freie primäre und/oder sekundäre Aminogruppen enthaltende Verbindungen bilden,

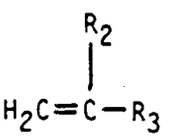
   wobei i) die Copolymeren der Komponente (A) intramolekular angebundene Carbonsäureanhydrid-Anteile enthalten, wobei das Anhydrid-Äquivalentgewicht der Copolymeren zwischen 393 und 9.800 liegt und (ii) die Bindemittelzusammensetzung 0,25 bis 10 Anhydrid-Anteile je blockierte Aminogruppe enthält.

2. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß Komponente (A) hauptsächlich aus einem Copolymeren von :

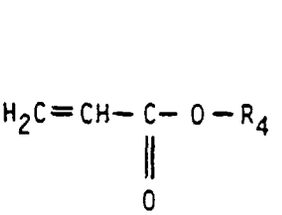
   a) 3 bis 25 Gewichtsteilen Maleinsäureanhydrid, und
   b) 75 bis 97 Gewichtsteilen von wenigstens einem copolymerisierbaren Monomeren entsprechend einer der folgenden allgemeinen Formeln (I), (II) und (III) besteht :



(I)



(II)



(III)

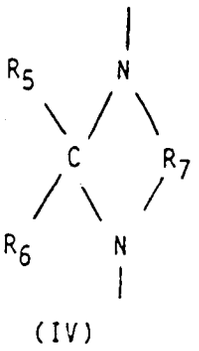
   in denen bedeuten :

   R_1 und R_4 unabhängig voneinander, je eine alifatische oder cycloalifatische C_1-C_{18}-Kohlenwasserstoffgruppe, in der ein oder mehrere Kohlenstoffatome durch ein Heteroatom, nämlich ein Sauerstoff-, Schwefel- oder Stickstoffatom, ersetzt sein kann (können),
   R_2 Wasserstoff, eine Methyl-, Ethyl-, Chlor- oder Fluorgruppe, und
   R_3 eine alifatische C_2-C_{15}-Kohlenwasserstoffgruppe, eine cycloalifatische C_5-C_{10}-Kohlenwasserstoffgruppe, eine aralifatische C_7-C_{18}-Kohlenwasserstoffgruppe oder eine aromatische C_6-C_{12}-Kohlenwasserstoffgruppe, wobei diese Gruppen ein oder mehrere Heteroatome aus der Gruppe bestehend aus einem Sauerstoff-, Schwefel- oder Stickstoffatom in Form einer Ether-, Ester-, Amid-, Urethan-, Harnstoff-, Thioester-, Oxiran-, Keton-, Lactam- oder Lactongruppe enthalten, und in denen Komponente (B) Aldimin, Ketimin, Oxazolan, Hexahydropyrimidin, Tetrahydroimidazol, Dihydroimidazol, Tetrahydropyrimidin, Amidacetal oder Amidaminal darstelt.

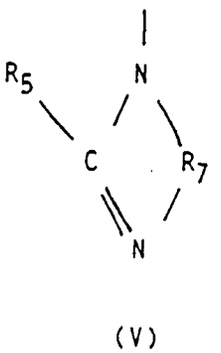
3. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 2, dadurch gekennzeichnet, daß die Maleinsäureanhydrid-Copolymeren (A) ein durch Gelchromatographie bestimmtes gewichtsdurchschnittliches Molekulargewicht [$\overline{M}w$] von 3.000 bis 50.000 aufweisen und ihr Anhydrid-Äquivalentgewicht (= in Gramm ausgedrückte Menge, die 1 Mol Anhydridgruppen enthält) zwischen 3.800 und 393 liegt.

4. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 2, dadurch gekennzeichnet, daß die Maleinsäureanhydrid-Copolymeren (A) Styrol-, Methacrylat- und/oder Acrylateinheiten enthalten.

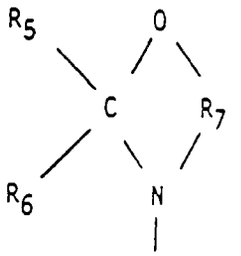
5. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß Komponente (B) ein statistisches Mittel von 1 bis 50 Struktureinheiten nach mindestens einer der folgenden allgemeinen Formeln (IV), (V), (VI), (VII), (VIII) und (IX) aufweist :



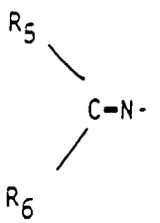
(IV)



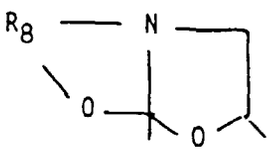
(V)



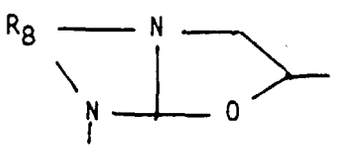
(VI)



(VII)



(VIII)



(IX)

in denen bedeuten :

R_5 und R_6, unabhängig voneinander, je Wasserstoff, eine alifatische C_1-C_{18}-Kohlenwasserstoffgruppe, eine cycloalifatische C_5-C_{10}-Kohlenwasserstoffgruppe, eine aralifatische C_7-C_{18}-Kohlenwasserstoffgruppe oder eine Phenylgruppe, oder
R_5 und R_6 zusammen die erforderlichen Atome zur Bildung eines fünf- oder sechsgliedrigen cycloalifatischen Ringes mit dem Kohlenstoffatom, mit dem sie gemeinsam verbunden sind, R_7 eine zweiwertige alifatische C_2-C_6-Kohlenwasserstoffgruppe, die jedoch nur eine Kette von 2 bis 3 Kohlenstoffatomen zwischen den definierten Heteroatomen des Ringes aufweist, R_8 eine zweiwertige alifatische C_2-C_{10}-Kohlenwasserstoffgruppe, die jedoch nur 2 bis 3 Kohlenstoffatome zwischen den Heteroatomen, mit denen diese Gruppe verbunden ist, aufweist.

6. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 5, dadurch gekennzeichnet, daß Komponente (B) ein Polyoxazolan ist, das dadurch erhalten ist, daß man ein Monooxazolan gemäß der allgemeinen Formel (V) mittels Wasserstoff auf dessen Stickstoffatom mit einem polyfunktionellen Reagens aus der Gruppe bestehend aus Polyisocyanat, Polyepoxid, Polycarbonsäure, teilweise veresterter Polycarbonsäure oder Polysäureanhydrid reagieren läßt.

7. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die ladungserzeugende Schicht als einziges Bindemittel ein oder mehrere, durch die Feuchtigkeitshärtung der gemischten Komponenten (A) und (B) erhaltene Harze enthält.

8. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die durch die Feuchtigkeitshärtung der gemischten Komponenten (A) und (B) erhaltenen Harze in Kombination mit wenigstens einem anderen, als Bindemittel dienenden Polymeren enthalten sind.

9. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 8, dadurch gekennzeichnet, daß das andere Polymere ein

Acrylatharz, ein Methacrylatharz, ein Copolyester eines Diols, mit Isophthal- und/oder Terephthalsäure, ein Polyacetal, ein Polyurethan, ein Polyesterurethan oder ein aromatisches Polycarbonat ist.

10. Fotoleitendes Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß der Träger ein Aluminiumträger ist oder ein mit einer eine leitfähige Schicht bildenden Aluminiumschicht überzogener Träger ist.

Revendications

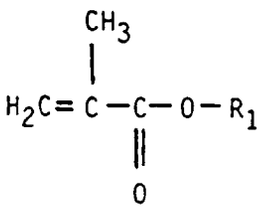
1. Un matériau d'enregistrement photoconducteur contenant un support et une couche générant des charges (CGC) en relation contigüe avec une couche transportant des charges (CTC) contenant un matériau transportant n-charges (n-MTC), caractérisé en ce que le liant de ladite couche générant des charges (CGC) est faite insoluble dans du chlorure de méthylène par réticulation, et est composé essentiellement d'une composition de liant durcie sous l'influence de l'humidité et préparée en mélangeant les composantes suivantes (A) et (B):

(A) 30 à 99 parties en poids d'au moins un copolymère de composés oléfiniquement insaturés ayant un poids moléculaire moyen en poids [$\overline{M}w$] d'au moins 1500 et contenant des fractions chimiquement incorporées capables de subir une réaction d'addition avec des groupes amino, et
(B) 1 à 70 parties en poids de substances organiques contenant des groupes amino neutralisés à partir desquelles substances sont formés - sous l'influence de l'humidité - des composés possédant des groupes amino libres primaires et/ou secondaires, et

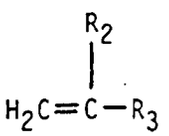
dans laquelle i) les copolymères de la composante (A) contiennent des fractions d'anhydride carboxylique liées intramoléculairement, le poids équivalent d'anhydride des copolymères étant de 393 à 9800 et ii) la composition du liant contient de 0,25 à 10 fractions d'anhydride pour chaque groupe amino neutralisé.

2. Matériau d'enregistrement photoconducteur selon la revendication 1, caractérisé en ce que ladite composante (A) se compose essentiellement d'un copolymère de:

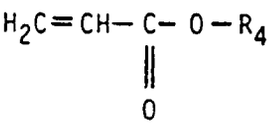
a) 3 à 25 parties en poids d'anhydride maléique, et
b) 75 à 97 parties en poids d'au moins un monomère copolymérisable qui correspond à une des formules générales suivantes (I), (II) et (III):



(I)



(II)



(III)

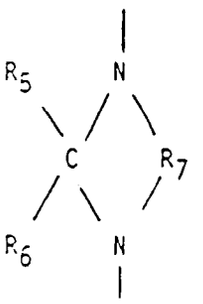
dans lesquelles:

R_1 et R_4, l'un indépendamment de l'autre, représentent chacun un groupe hydrocarbure aliphatique ou cycloaliphatique en C_1-C_{18}, dans lequel un ou plusieurs atomes de carbone peuvent être remplacés par des hétéroatomes choisi du groupe composé d'oxygène, de soufre et d'azote,
R_2 représente un atome d'hydrogène, un groupe méthyle, un groupe éthyle, un atome de fluor ou un atome de chlore, et R_3 est un groupe hydrocarbure aliphatique en C_2-C_{15}, un groupe hydrocarbure cycloaliphatique en C_5-C_{10}, un groupe hydrocarbure araliphatique en C_7-C_{18}, un groupe hydrocarbure aromatique en C_6-C_{12} contenant un ou plusieurs hétéroatomes choisi du groupe composé d'oxygène, de soufre et d'azote sous la forme d'un groupe éther, ester, amide, uréthane, urée, thioester, oxirane, cétone, lactame ou lactone; et caractérisé en ce que la composante (B) est un composé choisi du groupe composé d'une aldimine, une cétimine, un oxazolane, une hexahydropyrimidine, un tétrahydroïmidazole, un dihydroïmidazole, une tétrahydropyrimidine, un amidacétal et un amidaminal.

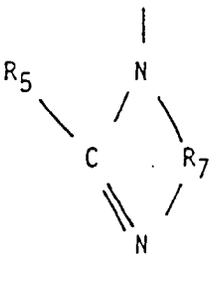
3. Un matériau d'enregistrement photoconducteur selon la revendication 2, caractérisé en ce que lesdits copolymères d'anhydride maléique (A) ont un poids moléculaire moyen en poids [$\overline{M}w$] déterminé par la chromatographie sur gel de 3000 à 50.000, et que leur poids équivalent d'anhydride (= la quantité en g contenant 1 mol de groupes anhydride) est de 3800 à 393.

4. Matériau d'enregistrement photoconducteur selon la revendication 2, caractérisé en ce que lesdits copolymères d'anhydride maléique (A) contiennent des unités de styrène, de méthacrylate et/ou d'acrylate.

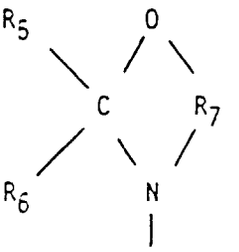
5. Matériau d'enregistrement photoconducteur selon la revendication 1, caractérisé en ce que la composante (B) contient une moyenne statistique de 1 à 50 unités structurales correspondant à au moins une des formules générales suivantes (IV), (V), (VI), (VII), (VIII) et (IX):



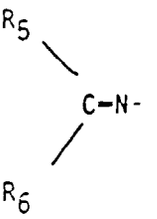
(IV)



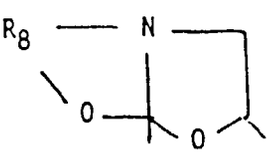
(V)



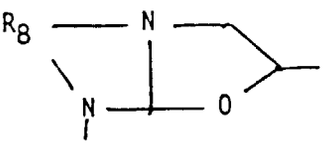
(VI)



(VII)



(VIII)



(IX)

dans lesquelles:

R_5 et R_6, l'un indépendamment de l'autre, représentent chacun un atome d'hydrogène, un groupe hydrocarbure aliphatique contenant 1 à 18 atomes de carbone, un groupe hydrocarbure cycloaliphatique contenant 5 à 10 atomes de carbone, un groupe hydrocarbure araliphatique contenant 7 à 18 atomes de carbone ou un groupe phényle, ou
R_5 et R_6 représentent ensemble les atomes nécessaires pour former un noyau cycloaliphatique pentagonal ou hexagonal avec l'atome de carbone auquel ils sont normalement liés, R_7 représente un groupe hydrocarbure aliphatique bivalent contenant 2 à 6 atomes de carbone, mais possédant seulement une chaîne de 2 à 3 atomes de carbone entre les hétéroatomes définis du noyau,
R_8 représente un groupe hydrocarbure aliphatique bivalent ayant 2 à 10 atomes de carbone, mais possédant seulement 2 ou 3 atomes de carbone entre les hétéroatomes auxquels ce groupe est lié.

6. Matériau d'enregistrement photoconducteur selon la revendication 5, caractérisé en ce que la composante (B) est un polyoxazolane que l'on obtient en laissant réagir un mono-oxazolane selon la formule générale (V) par l'hydrogène sur son atome d'azote avec un réactif polyfonctionnel choisi parmi un polyisocyanate, un polyépoxyde, un acide polycarboxylique, un acide polycarboxilique partiellement estérifié ou un anhydride de polyacide.

7. Matériau d'enregistrement photoconducteur selon la revendication 1, caractérisé en ce que ladite couche générant des charges contient comme seul liant une ou plusieurs résines obtenues par une réaction de durcissement par l'humidité des composantes mélangées (A) et (B).

8. Matériau d'enregistrement photoconducteur selon la revendication 1, caractérisé en ce que lesdites résines obtenues par une réaction de durcissement par l'humidité des composantes mélangées (A) et (B) sont présentes en combinaison avec au moins un autre polymère faisant fonction de liant.

9. Matériau d'enregistrement photoconducteur selon la revendication 8, caractérisé en ce que ledit autre polymère est choisi du groupe composé d'une résine d'acrylate, d'une résine de méthacrylate, d'un copolyester d'un diol avec de l'acide isophtalique et/ou téréphtalique, d'un polyacétal, d'un polyuréthane, d'un polyester-uréthane et d'un polycarbonate aromatique.

10. Matériau d'enregistrement photoconducteur selon la revendication 1, caractérisé en ce que ledit support est composé d'aluminium ou est un support muni d'une couche d'aluminium formant un revêtement conducteur.