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3,245,786

PHOTOCONDUCTIVE RECORDING MATERIALS

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18 Claims. (Cl. 96—1)

The present application is a continuation-in-part of application Serial No. 171,781, filed January 2, 1962, now abandoned.

This invention relates to a recording material comprising a photoconductive member which contains photoconductive zinc oxide dispersed in a binding agent and to a process for increasing the dark-resistivity of photoconductive zinc oxide.

Among the different photoconductive inorganic and organic compounds which already have been proposed to be employed in the manufacture of photoconductive layers for electrophotographic material, zinc oxide is one of the most interesting, among others because of its relatively low cost, its colourlessness, its easy manageability and the possibility of influencing its spectral sensitivity. In addition to these different properties which are not to be underestimated, zinc oxide, however, in its hitherto known forms, possesses the less interesting property of having a relatively low dark-resistivity. Hence the problem arises to make a photoconductive layer by means of photoconductive zinc oxide, whereby the electric conductivity of said photoconductive layer is sufficiently small in the dark for permitting an electrostatic charge, which is applied to said photoconductive layer to remain thereon for a sufficiently long time, e.g. the time normally needed for exposure to form an electrostatic latent image and to render it visible or to transfer it.

In this way, it has already been proposed, in connection with another photoconductor with relatively low specific resistivity viz. selenium, to use in the manufacture of the photoconductive layer a dispersion of the photoconductor in a binding agent with very high specific electric resistivity; such method has been described i.a. in Dutch patent specification 95,533. If a sufficiently large amount of binding agent is used the specific conductivity of which is much smaller than that of the photoconductor, it is possible to obtain a photoconductive layer which has a sufficiently high dark-resistivity. In practice, starting from zinc oxide (which has from its own a low specific resistivity), a photoconductive layer with a volume resistivity of 10^{13} ohm-cm. can be obtained by adding silicone resin having a specific resistivity of 10^{15} to 10^{16} ohm-cm. (see Hauße, Angew. Chem. 72 (1960), p. 735). It appears clearly from the fact that the specific resistivity of the mixture of zinc oxide and silicone resin is lower than that of the silicone resin, that zinc oxide has a lower specific resistivity than the silicone resin alone.

The effectiveness, however, of the just mentioned proposal is limited by factors inherent to the method involved. Indeed, it is evident that the sensitivity of a photoconductive material is direct in proportion to the quantity of the photoconductive substance, i.e. in inverse proportion to the quantity of binding agent with high resistivity present in the photoconductive layer. In prac-

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tice about 1 to 2 parts by weight of zinc oxide for 1 part by weight of binding agent is mostly used. If markedly higher amounts of binding agent are incorporated into the photoconductive layer, a photoconductive layer is obtained the sensitivity of which is too low for practical use.

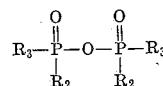
Further, in order to form a photoconductive layer with sufficiently high dark-resistivity in the above way, it does not suffice to add a binding agent the electric conductivity of which is only a little smaller than that of the photoconductor. Instead thereof a binding agent is to be employed the electric conductivity of which is so small that by adding it to the photoconductor, the mixture possesses a considerably higher dark-resistivity than the photoconductor itself. As a result a large series of macromolecular compounds which are very suitable for the rest to be used as a binding agent e.g. because of their low cost and good mechanical characteristics and/or characteristics for easy coating such as adhesive power on the support, pigment binding power and solubility, is excluded in advance. Concerning the limited group of remaining binding agents with sufficiently high dark-resistivity, there has to be remarked that most of them are not suited for application on a large scale, among others because of their poor mechanical properties and/or properties for easy coating and because of their high cost such as silicone resin mentioned by Hauße as example of a binding agent with high resistivity.

It is an object of the present invention to provide a completely new method for increasing the dark-resistivity of photoconductive zinc oxide. It is a further object to provide a new recording material with improved image-recording properties.

The recording material according to the invention comprises a photoconductive member containing photoconductive zinc oxide dispersed in a binding agent, and is characterized thereby that in said photoconductive member or/and in a member in intimate contact therewith has been incorporated an organic phosphorus compound according to one of the following general formulae (or tautomeric structures thereof):



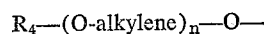
or



wherein:

R_1 represents a hydrogen atom, a metal atom, an ammonium group or an onium group such as a quaternary ammonium group, a halogen atom such as a chlorine atom, or a $\text{M}-\text{O}-$ group wherein M represents a hydrogen atom, a metal atom, an ammonium group or an onium group such as a quaternary ammonium group;

R_2 represents a halogen atom such as a chlorine atom, a $\text{M}-\text{O}-$ group (wherein M has the same significance as above), an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an alkoxy group, a substituted alkoxy group, an



radical (wherein R_4 represents an alkyl radical, an alkaryl radical, an amide group or an acyl group, and n represents an integer of between 1 and 50), an aryloxy group, a substituted aryloxy group, an ester group, an amino group, a substituted amino group such as a monoalkyl amino group, a dialkyl amino group or an acyl amino group, and

R_3 represents an alkyl radical, a substituted alkyl radical, a phenyl radical, an alkoxy radical, a substituted alkoxy radical, an $R_4-(O-alkylene)_n-O-$ radical (wherein R_4 and n have the same significance as above), an aryloxy group, a substituted aryloxy group, an ester group, an amino group, a substituted amino group such as a monoalkyl amino group, a dialkyl amino group or an acyl amino group.

In carrying out the present invention, it is necessary that the zinc oxide is allowed to come in contact with at least one of the compounds pertaining to one of the above mentioned classes (these compounds will be cited as "the compounds involved"). The contacting of the zinc oxide with the compound(s) involved can take place at any of the stages of the manufacturing process of the recording material. The contacting can take place before or during the preparation of the coating composition from which the photoconductive layer is formed, as well as after the application of the coating onto a support.

Although the increase of the dark-resistivity according to the invention can be obtained by contacting the zinc oxide with the compound involved in acid form as well as in salt form, the compound in acid form being preferably used.

In order to achieve an optimum effect, the compounds involved are preferably used dissolved or dispersed in a liquid.

Further, for increasing the dark-resistivity of the zinc oxide, the phosphorus compounds according to the above general formulae may be used in combination with one or more compounds in their acid or salt form pertaining to the following classes:

- (1) Unsubstituted aliphatic mono- and polycarboxylic acids and their anhydrides, containing no more than 10 carbon atoms in a straight line;
- (2) Aliphatic mono- and polycarboxylic acids which are substituted by water-solubilizing groups, such as a hydroxyl group or a carbonyl group;
- (3) Aliphatic mono- and polysulfonic acids;
- (4) Aliphatic boric acid compounds;
- (5) Aromatic mono- and polycarboxylic acids and their anhydrides;
- (6) Aromatic sulfonic acid compounds.

Compounds belonging to the first class are e.g.: acetic acid, propionic acid, acrylic acid, crotonic acid, capric acid, oxalic acid, malonic acid, adipic acid, succinic acid, maleic acid, fumaric acid, 1,1-cyclopropane dicarboxylic acid, acetic anhydride, maleic anhydride and succinic anhydride.

Compounds belonging to the second class are e.g.: lactic acid, tartaric acid, citric acid, saccholactic acid, α -hydroxy caproic acid, 9,10-dihydroxy stearic acid, 2,3-dihydroxy stearic acid, levulinic acid, 2-hydroxy valeric acid and 2-hydroxy-4-methyl-valeric acid.

Compounds belonging to the third class are e.g.: methane sulfonic acid and 1-butane sulfonic acid.

Compounds belonging to the fourth class are e.g.: monododecyl boric acid and monononadecyl boric acid.

Compounds belonging to the fifth class are e.g.: pyromellitic acid, 4,4'-stilbene dicarboxylic acid and phthalic anhydride.

Compounds belonging to the sixth class are e.g.: benzene sulfonic acid, toluene sulfonic acid and 2,2'-stilbene disulfonic acid.

In this respect it is to be mentioned that the aliphatic dicarboxylic acids mentioned above possess good dis-

persing properties for zinc oxide in organic solvents such as toluene and ethanol; for this reason in many cases one of the aliphatic dicarboxylic acids mentioned above is used in combination with the one of the phosphorus compounds according to the invention. The choice of the dicarboxylic acid is determined by the binding agent and the solvent used therefor. When ethanol is used as a solvent succinic acid is preferably used.

It has been established that in the most cases the adsorption of the compounds involved (especially those used in acid form) onto the surface of the zinc oxide grain occurs very fast. In order to obtain the desired effects it is, however, not necessary that the action of the compound involved onto the zinc oxide, occurs all over the available surface, or that all grains or clusters of grains undergo this action. The desired effect indeed is also obtained if the photoconductive layer is prepared starting from a mixture of untreated photoconductive zinc oxide and a photoconductive zinc oxide treated according to the present invention.

The following methods can successfully be applied in performing the present invention.

(1) In a column or in a rotating drum the compound involved is allowed to react in gaseous form onto the zinc oxide. Then the zinc oxide is dispersed in a solution or a dispersion of the binding agent. As a matter of course, only compounds having a low boiling point are considered.

(2) The compound involved is added to an aqueous dispersion of the zinc oxide. The treated zinc oxide is filtered off or centrifuged, dried and then dispersed in a solution of a binding agent. This method is especially suited for compounds which are soluble or dispersible in water.

(3) The zinc oxide is dissolved or dispersed in an organic solvent wherein the compound involved is soluble or dispersible, whereupon the necessary amount of the compound is added. Hereupon a binding agent can be added immediately.

(4) The zinc oxide, a binding agent and a solvent for the latter are dispersed together e.g. by grinding in a ball mill for 2 to 36 hours according to the particular size desired. One or more of the compounds involved are added before, during or after grinding.

(5) Onto a paper support a layer is applied from a composition which contains one or more of the compounds involved to which a binding agent may be added. Alternatively, the paper is imbibed, e.g. during its manufacture with such compound. On top of this layer a second layer is applied which contains untreated zinc oxide and a binding agent. During coating of the latter layer and/or during the storage of the material, the acid diffuses from the first layer to the zinc oxide and is adsorbed thereon. This process permits to reach a double effect. Indeed, when using a compound having acid properties and having also a pronounced antistatic character, the dosing can be regulated in such a way, that a sufficient amount of such compound is left in the first layer, so that this layer is sufficiently conductive for permitting a charge to be carried off during exposure.

(6) Onto a paper backing is firstly applied a layer of untreated zinc oxide which is dispersed in a binding agent. On top of this layer a layer is applied which contains one or more of the compounds involved and a binding agent if desired. During coating of the layer and/or during the storage of the material, this compound diffuses from the second layer to the zinc oxide in the first layer. By suitably choosing the binding agents for the second layer e.g. the adhesion of the developing powder can either be enhanced, resulting in an improved fixing of the powder, or can be decreased, resulting in a better powder transfer.

The dark-resistivity of the photoconductive zinc oxide layers according to this invention increases to an optimum value by using increasing quantities of the compound involved. By exceeding the amount, which gives an opti-

imum dark-resistivity, the latter decreases proportionally to the amount added beyond the optimum amount.

From the experiments it has been established that an optimum dark-resistivity is obtained by adding to the composition of the photoconductive layer during its manufacture, according to the nature of the compound involved (molecular weight, degree of acidity, solubility) 0.1 to 10% by weight of such compound (when used in acidic form), based on the weight of the photoconductive zinc oxide (preferably 0.1 to 3% of an acidic compound is used); the amount of the salts or neutralized acids above is normally markedly higher for obtaining the same effect as with the free acids, and can vary between 0.5 to 40%.

It is obvious that if the compound involved is added to a layer or sheet adjacent to the photoconductive layer, the compound is to be used in greater quantity, which can amount to 10% based on the weight of photoconductive zinc oxide.

It can be demonstrated that, when treating the zinc oxide grains by intimately contacting them with the cited amounts of one of the compounds involved and by measuring the resistivity in a measuring cell as described by W. Simm, *Chemie-Ingenieur-Technik* 31 (1959), 44, the dark-resistivity of the so treated zinc oxide was higher than that of the untreated zinc oxide.

In the manufacture of the photoconductive recording material according to the present invention, the photoconductive layer is coated from a composition containing the zinc oxide and a binding agent.

The ratio of insulating binding agent and photoconductor depends on the aimed quality of the photoconductive layer with respect to the photoconductive properties, mechanical strength and insulating power. The best results are obtained with a ratio of binding agent to photoconductor of 1:3 to 1:9; if layers are used with a relatively high amount of binding agent, the image-sharpness decreases; in general it is not possible to obtain useful results if the photoconductive layer does not consist for at least 50% of zinc oxide; if layers are used with a much lower content of binding agent, the mechanical strength of the coating may become insufficient.

The photoconductive recording material according to the present invention is suited for being used in the application of the mostly varying reproduction methods; one of the characterizing properties consists therein that very contrasty images can easily be obtained, and this in a very reproducible way, even in the most differing circumstances such as those caused by strongly varying degree of humidity of the air.

It has not yet been explained with certainty of which kind the phenomena are which take place during the contact of the zinc oxide with the compounds used according to the invention. The scope of this invention is thus by no means limited by the exposition set forth below which has only the purpose of giving an acceptable explanation of the observed phenomena.

It may be assumed with a certain probability, that the adsorption of the compound involved to the zinc oxide grains results in a decrease of the electric leak in and around the grain surface of the zinc oxide. There is no question here of hydrophobizing the zinc oxide grains in the usual sense, which is proved by the fact that the increase of the dark-resistivity can also be obtained e.g. with a water-soluble phosphoric acid derivative having antistatic properties such as an acid phosphate neutralized with one or more amines.

In any way it is an unexpected effect that by treating the zinc oxide with an antistatic the dark-resistivity is increased.

In order to establish the increase of the dark-resistivity obtained according to the process of the present invention, the dark-resistivity of the photoconductive layers is measured.

The dark-resistivity of an electrophotographic layer consisting of a powdery photoconductor which is dispersed in a binding agent, can be measured with ohmic contacts or with blocking contacts. The decision which method should be used is determined by the application of the material, in an electrolytic or xerographic reproduction method. If an electrolytic method of development is used, such as that described in the Belgian Patent No. 561,403, the first method is applied. For electrostatic methods of development such as those mentioned in the present invention, the method of the blocking contacts meets in the best way the conditions of practical use. The procedure is the following:

Photoconductive zinc oxide dispersed in a binding agent is coated on a backing having a relatively high conductivity such as paper or metal. The so obtained material is called hereinafter the electrophotographic material. The thickness of the photoconductive layer amounts to 10 to 15 μ . This material is stored for 15 h. in the dark and is then conditioned in the required circumstances of humidity and temperature. The electrophotographic material is then laid with its conductive backing on an earthened metal plate and then by means of a corona apparatus which is connected to the negative pole of a high tension source of 6,000 to 7,000 volts, electrostatically charged till saturation, which in most cases is reached after 5 to 10 seconds. The material is now taken away from the earthened plate and the dark-decay is then continuously registered, e.g. by means of an electrometer with vibrating electrode such as that described by C. J. Young and H. G. Greig, *RCA Review* (1954), XV, 469, switched to a recorder. The measuring of the field strength F , present on the photoconductive layer, begins precisely 5 seconds after completing the corona-charging. The measuring results are expressed in volts/cm. The relaxation-time, i.e. the time which passes from the beginning of the measuring whereby a field strength F_0 is measured till the moment wherein this value is decreased to F_0/e (e is the base of the natural logarithms), as well as the field strength are read on the dark-decay curve.

The Maxwell relation:

$$\tau = \epsilon \cdot \epsilon_0 \cdot \rho$$

wherein:

τ represents the relaxation-time in seconds,

ϵ represents the dielectric constant of the layer measured at 1 kc. (ϵ varies mostly from 2.5 to 5 in the layers which are considered here),

ϵ_0 represents the dielectric constant of the vacuum viz. 10^{-13} sec./ohm-cm., and

ρ represents the dark-resistivity of the layer in ohm-cm., gives the relation between the relaxation-time, the dielectric constant and the dark-resistivity.

The dark-resistivity of the layer in ohm-cm., represented by ρ is easily calculated from the following formula:

$$\rho = \frac{\tau}{\epsilon \cdot \epsilon_0}$$

In order to compare the results, it can simply suffice to use ρ as a comparative value for the dark-resistivity since the product $\epsilon \cdot \epsilon_0$ remains approximately constant.

For demonstrating the scope of the present invention as clearly as possible, some results of experimental measurements are listed hereinafter in Tables I and II.

It has to be mentioned that for the manufacture of the materials 4, 5 and 6 from Table I and for all the materials from Table II, ethanol has been used as solvent for the binding agent of the photoconductive layer. For the materials 1, 2 and 3 from Table I, methylene chloride has been used as a solvent. On manufacturing the materials 3 and 6 from Table I and of material 3 from Table II, the acid was added to the dispersion of the zinc oxide in the binding agent. For manufacturing material 4 from Table II, the zinc oxide was treated with the acid prior to adding the binding agent.

TABLE I

Test	Composition of the photoconductive layer in relative amounts by weight				Thickness of the photoconductive layer in μ	Relaxation time in seconds determined at 20° C. and 44% of relative humidity
	Binding agent A	Binding agent B	Zinc oxide	Monobutyl phosphate		
1	50				13	>3,600'
2	50		100		15	60'
3	50		100	0.5	15	240'
4		10			9	720
5		10	100		10	180
6		10	100	0.5	10	1,200

Binding agent A: Polyester of fumaric acid and 2,2-bis(p-hydroxyphenyl)-propane, prepared as described in the Belgian patent specification 563,173.

Binding agent B: A polyvinylbutyral containing 18.2% of non-acetalized vinyl alcohol units.

TABLE II

Test	Composition of the photoconductive layer in relative amounts by weight			Thickness of the photoconductive layer in μ	ϵ	τ (relative value) relaxation time	
	Binding agent ¹	Zinc oxide	Monobutyl phosphate			45% of relative humidity	70% of relative humidity
1	100			13	2.5	1	0.9
2	100	375		17	4.5	0.1	0.1
3	100	375	2.5	18	4.4	5	4.6
4	100	375	15	19		5.6	2.0
5	100		2.5	12	2.7	0.2	0.2

¹ A copolymer containing 85 parts vinyl acetate to 15 parts vinyl stearate.

From the results obtained the following can be concluded:

(1) The relaxation time of a layer only consisting of binding agent (Table I, tests 1 and 4, and Table II, test 1) is markedly larger than that of a layer containing the same binding agent and a photoconductive zinc oxide of the usual type (Table I, tests 2 and 5, and Table II, test 2); this observation applies to the three different binding agents listed in Tables I and II. This means that a charge which is applied on a layer consisting of a binding agent and zinc oxide, flows away more quickly than the charge applied on a layer which consists exclusively of binding agent. This points out that the zinc oxide of the usual type possesses a markedly lower resistivity than the binding agent. This establishment fully agrees with that observed by Hauße, when adding zinc oxide to a silicone resin (Ang. Chem. 72 (1960), 735).

(2) The relaxation time of a layer which only consists of binding agent (Table I, tests 1 and 4, and Table II, test 1) depending on the kind of the binding agent used, can be higher (Table I, test 1) as well as lower (Table I, test 4, and Table II test 1) than that of a layer which contains the same binding agent and a photoconductive zinc oxide, which according to the present invention was contacted with a compound having acid properties (Table I, tests 3 and 6, and Table II, tests 3 and 4). In the latter case (binding agent wherein a photoconductor is dispersed having a greater relaxation time than the binding agent alone) the specific dark-resistivity of the photoconductive layer containing this photoconductor is larger than that of the binding agent.

From the preceding tests it can be concluded that the binding agents can be divided into two groups according to whether the specific dark-resistivity is higher or lower than the specific dark-resistivity of the treated zinc oxide.

Further on in this specification a list of binding agents divided into classes, is given. Referring to that list, the binding agents follow now the specific resistivity of which has been examined with regard to the zinc oxide.

Binding agents belonging to the group of those possessing a higher specific dark-resistivity than the treated zinc oxide are:

The compounds *a*, *b*, *c* and *d* from class A,

The compounds *a*, *b* and *c* from class B-I,

The compounds *a*, *b*, *c*, *d*, *e* and *f* from class B-III,

The compounds *a*, *d*, *e*, *f*, *g* and *h* from class B-IV,

The compounds *a*, *b*, *c* and *d* from class B-V,

The compounds *a*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, *j* and *k* from class C,

The compounds *a*, *b*, *c*, *d*, *e*, *f* and *g* from class D.

35 Binding agents belonging to the group of those possessing a lower specific dark-resistivity than the treated zinc oxide are:

The compounds *e*, *f*, *g* and *h* from class A,

40 The compounds *a*, *b*, *c*, *d* and *e* from class B-II,

The compounds *b*, *c* and *i* from class B-IV,

The compounds *a*, *b* and *c* from class B-VI,

The compound *b* from class C.

The latter binding agents thus possess no pronounced high specific electric resistivity and hence were not considered formerly as binding agents usable for photoconductive compounds such as zinc oxide.

It appears therefrom that when applying the process according to the present invention, it becomes possible to use binding agents which could not be used formerly because of their too low specific resistivity.

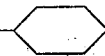
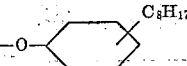
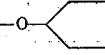
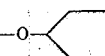
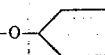
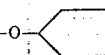
The treatment of the zinc oxide according to the present invention thus permits the use of binding agents in the manufacture of photoconductive layers, the dark-resistivity of which, measured on layer thicknesses of from 5 to 15 μ as usual in electrophotography, does not suffice in itself for carrying a sufficient electrostatic charge, especially by relative humidities of the air higher than 50 to 60%. If zinc oxide powder is added to such a binding agent in a known way, the dark-resistivity of the layer measured at e.g. 60% of relative humidity, is not improved. It does however, improve, if according to the present invention, the zinc oxide is treated with a phosphorus compound represented by the given general formulae. Finally it is possible by applying the present invention to force up strongly the ratio of the zinc oxide to the binding agent (e.g. till 7 parts by weight of zinc oxide for one part by weight of binding agent) which enables to manufacture more sensitive photoconductive layers.

Phosphorus compounds corresponding to the above general formulae and which increase the dark-resistivity of photoconductive zinc oxide are given below by way of illustration. The identified compounds have an acid character. Their salts can be obtained by neutralization with

a known base or by reaction with a metal hydroxide or with a metal carbonate.

Some of these compounds are marketed under their chemical name or under a trade name as is given. Other compounds were prepared according to methods known from the literature or according to a method which is given here.

Nitrogen-containing derivatives or phosphoric acid according to the general formulae such as amido phosphates are among others described by G. M. Kosalopoff in Organophosphorus Compounds, John Wiley & Sons, Inc., New York, U.S.A., p. 305. Acid acyl phosphites, acid acyl phosphates and acid esters of pyrophosphoric acid are also described, respectively on pages 348, 349 and 350.

No.	R ₁	R ₂	R ₃
1	-OH	-OH	-O-CH ₃
2	-OH	-OH	-O-C ₂ H ₅
3	-OH	-OH	-O-C ₃ H ₇
4	-OH	-OH	-O-CH ₂ -CHOH-CH ₂ OH
5	-OH	-OH	
6	-OH	-OH	
7	-OH	-OH	-CH ₂ Cl
8	-OH	-O-CH ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃
9	-OH	-O-CH ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₇ =CH-CH ₃ (CH ₂) ₇ -CH ₃
10	-OH	-O-C ₅ H ₁₁ (iso)	-O-C ₅ H ₁₁
11	-OH	-O-C ₅ H ₁₁ (iso)	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
12	-OH	-O-(CH ₂ -CH ₂ -O) ₇ -CH ₂ -CH ₂ -O-CH ₂ -oleyl	-O-(CH ₂ -CH ₂ -O) ₇ -CH ₂ -CH ₂ -O-CH ₂ -oleyl
13	-OH		
14	-OH	-H	CH ₃ C-NH-CH ₂ -(CH ₂) ₁₀ -CH ₃ CH ₃
15	-OH	-OH	-O-(CH ₂) ₃ -CH ₃
16. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	
(a)	-OH	-OH	
(b)	-OH	-O- 	
17. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	-O-CH ₂ -(CH ₂) ₁₄₋₁₆ -CH ₃
(a)	-OH	-O-CH ₂ -(CH ₂) ₁₄₋₁₆ -CH ₃	-O-CH ₂ -(CH ₂) ₁₄₋₁₆ -CH ₃
(b)	-OH	-O-CH ₂ -(CH ₂) ₁₄₋₁₆ -CH ₃	-O-CH ₂ -(CH ₂) ₁₄₋₁₆ -CH ₃
18. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	-O-CH ₃
(a)	-OH	-O-CH ₃	-O-CH ₃
19. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	-O-CH ₃
(a)	-OH	-O-CH ₃	-O-CH ₃
20. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	-O-C ₂ H ₅
(a)	-OH	-O-C ₂ H ₅	-O-C ₂ H ₅
21. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:	-OH	-OH	-O-C ₂ H ₅
(a)	-OH	-O-C ₂ H ₅	-O-C ₂ H ₅
(b)	-OH	-O-C ₂ H ₅	-O-C ₂ H ₅
22. Mixture of mono- and dihydroxy compounds (1:1):	-OH	-OH	-O-C ₃ H ₇ (iso)
(a)	-OH	-O-C ₃ H ₇ (iso)	-O-C ₃ H ₇ (iso)
23. Mixture of mono- and dihydroxy compounds:	-OH	-OH	-O-C ₄ H ₉
(a)	-OH	-O-C ₄ H ₉	-O-C ₄ H ₉
24. Mixture of mono- and dihydroxy compounds:	-OH	-OH	-O-C ₅ H ₁₁
(a)	-OH	-O-C ₅ H ₁₁	-O-C ₅ H ₁₁
25. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:	-OH	-OH	-O-C ₅ H ₁₁ (iso)
(a)	-OH	-O-C ₅ H ₁₁ (iso)	-O-C ₅ H ₁₁ (iso)
26. Mixture of mono- and dihydroxy compounds:	-OH	-OH	-O-C ₅ H ₁₁
(a)	-OH	-O-C ₅ H ₁₁	-O-C ₅ H ₁₁
(b)	-OH	-O-C ₅ H ₁₁	-O-C ₅ H ₁₁

No.	R ₁	R ₂	R ₃
27. Mixture of mono- and dihydroxy compounds:			
(a)-----	-OH	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃
(b)-----	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₂ -CH ₃
28. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:			
(a)-----	-OH	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃
(b)-----	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₂ -CH ₃
29. Mixture of mono- and dihydroxy compounds (1:1):			
(a)-----	-OH	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
(b)-----	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
30. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:			
(a)-----	-OH	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
(b)-----	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
31. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:			
(a)-----	-OH	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
(b)-----	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅
32. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:			
(a)-----	-OH	-OH	-O-CH ₂ -(CH ₂) ₈ -CH ₃
(b)-----	-OH	-O-CH ₂ -(CH ₂) ₈ -CH ₃	-O-CH ₂ -(CH ₂) ₈ -CH ₃
33. Mixture of mono- and dihydroxy compounds (1:1):			
(a)-----	-OH	-OH	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃
(b)-----	-OH	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃
34. Mixture of mono- and dihydroxy compounds, the amount of mono-hydroxy compound being larger than that of the dihydroxy compound:			
(a)-----	-OH	-OH	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃
(b)-----	-OH	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃	-O-CH ₂ -(CH ₂) ₁₀ -CH ₃
35.-----	-OH	-O-CH ₃	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
36.-----	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
37.-----	-OH	-O-C ₈ H ₁₇	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
38.-----	-OH	-O-C ₈ H ₁₇	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
39.-----	-OH	-O-CH ₂ -CH-(CH ₂) ₃ -CH ₃ C ₂ H ₅	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
40.-----	-H	-O-CH ₃	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
41.-----	-H	-O-(CH ₂) ₃ -CH ₃	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
42.-----	-Cl	-Cl	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
43.-----	-OH	-O-CH ₂ -(CH ₂) ₂ -CH ₃	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃
44.-----	-OH	-O-C ₂ H ₅	-O-CH ₂ -(CH ₂) ₁₁ -CH ₃

The compound under No. 5 is prepared as described in Ann. 181 (1876), p. 181.

The compound under No. 14 is prepared by reacting lauryl amine with hypophosphorous acid in a medium of acetone. Melting point: about 190° C.

The compound under No. 15 is prepared by hydrolysis of the corresponding dichloride, prepared according to the method described in J. Chem. Soc. (1940), II, p. 1446. After the hydrolysis, the water and the formed hydrochloric acid are separated under vacuum. The last traces

of water are removed by drying the obtained product in a vacuum exsiccator over phosphorus pentoxide.

The compound under No. 43 is prepared as described in J. Chem. Soc. (1944), I, p. 88.

The compounds identified above have an acid character. Their salts can be obtained by neutralization with a known base or by reaction with a metal hydroxide, a metal amide or a metal carbonate. The most suited salts for increasing the dark-resistivity of a photoconductive zinc oxide layer comprise an alkaline-earth metal ion e.g. a calcium or a barium ion or a metal ion e.g. a copper ion, a zinc ion, a cobalt ion or a chromium ion. The zinc salts are preferably formed "in situ" with the photoconductive zinc oxide during the manufacture of the photoconductive layer.

Although according to the invention the phosphorus compounds are preferably used, in acid form or in the form of one of the metal salts mentioned first herein before it is also possible to use the corresponding ammonium or organic quaternary ammonium salts such as an acid phosphate neutralized with one or more amines.

The phosphorus compounds according to one of the general formulae are generally preferred to the compounds of the other classes. Among these latter compounds, the aliphatic dicarboxylic acids and hydroxy-substituted monocarboxylic acids seem to be the most interesting. The aromatic compounds, however, belonging to the two last classes, generally show a less favorable action than the compounds from the first five classes.

The preferably used combination is that of a phosphorus compound according to one of the general formulae with an aliphatic dicarboxylic acid such as succinic acid.

The amount of aliphatic dicarboxylic acid which is preferably used in combination with the acid phosphorus compound varies from 0.1 to 1% by weight of the zinc oxide.

In the manufacture of the recording material according to the present invention, in practice any commercially available zinc oxide type prepared according to the "French Process" (by oxidation of zinc vapour) can be used.

Binding agents for the zinc oxide photoconductor suited for the manufacture of recording material according to the present invention are among others described in Dutch Patent No. 95,533 and the Belgian Patents Nos. 533,514 and 587,301. The halogenated polymers and polycondensates described in Belgian Patent No. 604,126 and the photoconductive polymers described in Belgian Patents Nos. 588,049 and 589,996 are also suited for this purpose. Further may be used as binding agents:

A. Natural substances and modified natural substances:

- (a) Colophony and esterified colophony,
- (b) Dammar resin,
- (c) Colophony modified with phenolformaldehyde resin,
- (d) A maleate resin based on colophony,
- (e) Ethylcellulose acetate,
- (f) Hydroxy ethyl cellulose acetate,
- (g) Cellulose aceto-stearate,
- (h) Ethyl cellulose stearate.

B. Vinyl polymers and substituted vinyl polymers:

I. Photoconductive vinyl polymers—

- (a) The vinyl polymers described in Belgian Patent No. 588,048.
- (b) The vinyl polymers described in Belgian Patent No. 588,050 such as copoly N-vinyl carbazole/ethyl acrylate (74.5/25.5).

II. Polyvinyl esters—

- (a) Vinyl acetate resin.
- (b) A copolymer of vinyl acetate and crotonic acid.
- (c) A copolymer of vinyl acetate and an ester of vinyl alcohol and a higher aliphatic carboxylic acid such as lauric acid, stearic acid, palmitic acid e.g. copolymers of vinyl acetate and vinyl stearate, a copolymer of vinyl acetate and vinyl

laurate in any of the following properties, respectively 80/20, 60/40, 50/50.

(d) Polyvinyl stearate.

(e) Copoly (vinyl acetate/maleic acid), prepared as follows: A solution of 300 g. of maleic anhydride, 258 g. of vinyl acetate and 1.12 g. of azo-bis-isobutyronitrile in 3 l. of thiophene-free benzene is heated for 9 h. at 75° C.

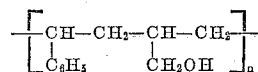
The flocculated polymer is sucked off and washed with methylene chloride. The obtained product is firstly dried by air at room temperature whereby the anhydride groups hydrolyse to acid groups. Hereupon follows drying at 40° C. Yield: 344 g.

III. Vinyl chloride polymers and copolymers—

- (a) A polyvinyl chloride.
- (b) A copolymer of vinyl chloride and vinyl isobutyl ether.
- (c) A copolymer of 91% vinyl chloride, 3% vinyl acetate and 6% vinyl alcohol.
- (d) A copolymer of vinyl chloride, vinyl acetate and maleic anhydride.

IV. Styrene polymers and copolymers—

- (a) A polystyrene.
- (b) A copolymer of styrene and monoisobutyl maleate.
- (c) Copoly (styrene/methacrylic acid) prepared as follows: A solution of 645 g. of methacrylic acid, 156 g. of styrene and 2 g. of azo-bis-isobutyronitrile in 800 cms. of carbon tetrachloride and 7.2 cm.³ of thiophene-free benzene is refluxed with stirring for 12 h. The formed precipitate is sucked off, washed with hexane and dried at 40–50° C.
- (d) Copoly (styrene/butadiene).
- (e) Copoly (dimethylitaconate/styrene).
- (f) A copolymer of the following structure



V. Polymers of methacrylic acid esters—

- (a) Poly(n-butylmethacrylate).
- (b) Polyalkylmethacrylate.
- (c) Polymers of methyl methacrylate.

VI. Polyvinylacetates and copolymers—

- (a) A vinyl butyral with 18.2% of vinyl alcohol.
- (b) A copolymer of vinyl butyral (80%) vinyl alcohol (17.5 to 21%) and vinyl acetate (0 to 2.5%).
- (c) A copolymer of vinyl formal with 5 to 6% vinyl alcohol and 9.5 to 13% of vinyl acetate.

C. Polycondensates:

- (a) Pentaerythrite phthalate.
- (b) A resinous terpene polybasic acid.
- (c) Polyester of phosphoric acid and hydroquinone.
- (d) Polyhydroquinone phenyl phosphonate.
- (e) Polyphosphite, prepared as follows: A mixture of 27.6 g. of diethyl phosphite, prepared as described in Inorg. Synth., vol. IV, p. 58, 15 g. of glycol and 13 mg. of anhydrous zinc acetate is heated in a large tube on a bath of propylene glycol (boiling point 177° C.). 23 cm.³ of ethanol are split off. After the distillation of this amount of ethanol, the tube is connected for 2 h. to a vacuum of 5 mm. of Hg. A bright-colored and viscous product is obtained.
- (f) Polyester of 2,2-bis(4-hydroxyphenyl)-propane and fumaric acid, prepared as described in Belgian patent specification 563,173.
- (g) Polyester of 4,4'-dicarboxy phenyl ether and 2,2-bis(4-hydroxyphenyl)-propane, prepared as described in the Belgian patent specification 563,173.
- (h) Polyester of 1,3-disulfobenzene and 2,2-bis(4-hydroxyphenyl)-propane, and the polyester of diphenyl-p,p'-disulphonic acid with 2,2-bis(4-hydroxyphenyl)-propane, prepared as described in the Belgian patent specification 565,478.

(i) Polyester of neopentyl-glycol with isophthalic acid, prepared as described in the Belgian patent specification 563,173.

(j) The polyesters described in Belgian patent specification 565,478 such as the polyester of 2,2-bis(4-hydroxyphenyl)-propane and diphenyl-p,p'-disulphonic acid.

(k) The polycarbonates described in Belgian patent specification 563,446 such as a polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane.

D. Synthetic resins and synthetic rubbers:

(a) Polyindene.

(b) Polycyclopentadiene.

(c) Silicone resins.

(d) 100% cyclic rubbers.

(e) Chlorinated polypropylene.

(f) A ketone resin prepared by condensation of an aliphatic ketone with formaldehyde.

(g) Ketone resins.

The choice of suitable binding agents is not limited to the previously polymerized compounds. Indeed, low molecular compounds or mixtures of low and high molecular compounds or of semi-polymerisates, which are polymerised or condensed in situ or which are cross-linked according to one of the methods known in polymer chemistry, may be used too.

To the compositions for forming the photoconductive layers according to the invention, suitable plasticizers can be added if desired such as dibutyl phthalate, dimethyl phthalate, dimethyl glycol phthalate, tricresyl phosphate, triphenyl phosphate, monocresyl diphenyl phosphate etc. in amounts varying from 10 to 30% by weight of the amount of binding agent.

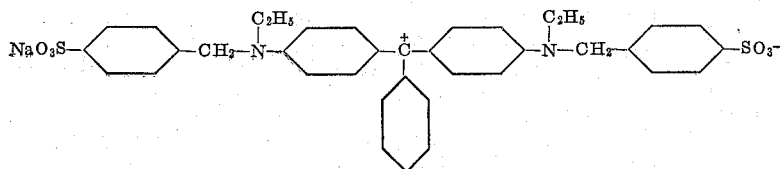
Other additives known in the art of coating technique may further be used e.g. pigments, compounds influencing gloss and viscosity, compounds counteracting ageing and oxydation or influencing the thermal stability of the layers. Those additives are preferred which do not markedly decrease the dark-resistivity of the photoconductive layer.

Finally, compounds which have occasionally photoconductive properties and which increase the general sensitivity and/or the sensitivity for electromagnetic rays from a determined part of the spectrum, can also be present in the photoconductive layers according to the invention.

In this way, the general sensitivity and/or the sensitivity for electromagnetic rays from the visible part of the spectrum can considerably be increased by adding to the photoconductive layer one or more compounds chosen from one or more of the following classes, preferably in an amount ranging from 0.1 to 5% based on the weight of the zinc oxide.

A. Triphenyl methane dyestuffs without ring-closure such as:

Malachite Green (C.I. 42,000); Brilliant Green (C.I. 42,040); Patent blue V (C.I. 42,045); Kiton blue A (C.I. 42,052); Xylene blue AS (C.I. 42,080); Naphthalene Green G (C.I. 42,085); Erioglaucine A supra (C.I. 42,090); Cyanol extra (C.I. 42,135); Fuchsine (C.I. 42,510); Crystal violet (C.I. 42,555); Crystal violet-base (C.I. 42,555 B); Methyl green 235 (C.I. 42,585); Fuchsine Acid (C.I. 42,685); Brilliant glacier blue (C.I. 664); Aurine (C.I. 43,800); Eriochrome Cyanine R (C.I. 43,820); Naphthaline green V (C.I. 44,025); Erio green B Supra (C.I. 44,025); Aurine tricarbonsäure ammoniumsalz (Z.A.); Chlorphenol Rot, Bromkresol Grün, Broomkresol Purp, Thymolblau and Bromthymolblau and the compound of the following formula:



B. Triphenylmethane dyestuffs with ring-closure such as:

Rhodamine G (C.I. 45,150); Rhodamine B (C.I. 45,170); Calcozine Red BX (C.I. 45,170); Erio Brilliant Fuchsine BBL (C.I. 45,190); Fast Acid Blue R (C.I. 45,205); Fluoresceine Sodium (C.I. 45,350); Eosine (C.I. 45,380); Phloxine BBN (C.I. 45,410 and C.I. 45,410 A); Diiodofluoresceine Sodium (C.I. 45,425 and C.I. 45,425 A); Erythrosine bluish (C.I. 45,430); Rose Bengale (C.I. 45,440 and C.I. 45,435); Galleine MS (S. 897); Acridine orange (C.I. 46,005); Phosphine E (C.I. 46,045); Dibromofluoresceine Sodium.

(1) C. Diarylmethane dyestuffs such as:

Auramine O (C.I. 41,000); Pyronine G (C.I. 46,005); Rhodamine S (C.I. 45,050); Acridine Yellow (C.I. 46,025).

D. Polymethine dyestuffs:

(1) Styryls, such as: 1-ethyl-4-[β-(3-N-ethylcarbazyl)-vinyl]-quinolinium chloride; 1-ethyl-2-[β-(3-N-ethylcarbazyl)-vinyl]-quinolinium iodide; methyl-bis[p-(1'-β'-hydroxyethyl-2'-quinolinium chloride)-vinyl]-phenylamine; tri-[p-(1'-β'-hydroxyethyl-2'-quinolinium chloride)-vinyl]-phenylamine; 1-ethyl-2-β-(p-methoxyphenyl)-vinyl-quinolinium-p-toluenesulfonate; 1-phenyl-3-[(β-phenyl)-vinyl]-5-phenyl-Δ-2-pyrazoline; 1-[β-hydroxyethyl]-2-[β-(p-dimethylaminophenyl)-vinyl]-quinolinium chloride; 1-ethyl-2-[β-(p-dimethylaminophenyl)-vinyl]-quinolinium iodide.

(2) Monomethine cyanines such as: {3-methyl-5-methylthio-1,3,4-thiadiazole}-{3-methylnaphtho-[2,1-d]-thiazole}-2,2'-monomethine cyanine iodide; 1,1'-diethyl-2,2'-thiacyanine bromide; {3-methylbenzothiazole}-{3-ethylnaphtho[2,1-d]-thiazole}-2,2'-monomethinecyanine-p-toluenesulfonate; 1,1'-diethyl-2'-methyl-6,6'-bis(dimethylamine)-2,4'-quinocyanine iodide; 1,1'-dimethyl-2,4'-quinocyanine iodide; Pinachrome (C.I. 807).

(3) Trimethine cyanines, such as: Pinacyanol (C.I. 808).

(4) Oxonols such as: 5,5'-bis[2-thio-3-ethylthiazolidine-2,4-dione]monomethine-oxonol; 4,4'-bis[1-(p-sulfophenyl)-3-methyl-5-pyrazolone]-α-methyl-trimethine-oxonol; 4,4'-bis[1-(p-sulfophenyl)-3-methyl-5-pyrazolone]-pentamethine-oxonol; Zolon Red, prepared according to the method of B. Gehauf and J. Goldensen described in Anal. Chem. 27 (1955), 420/21.

(5) Merostyryls such as: 1-p-sulfophenyl-3-methyl-4-(p-dimethylaminobenzylidene)-5-pyrazolone; 1-[1',5'-(disulfo)-naphthyl-3']-3-(1-heptadecyl)-4-4'-quinolylmethylidene-5-pyrazolone.

(6) Merocyanines such as: Juane quinoline; 2-thio-3-ethyl-5-(3-ethyl-2-benzothiazolinyldene)-thiazolidine-dione; the triethylamine salt of 2-thio-3-ethyl-5-(3-ω-sulfobutyl-2-benzothiazolinyldene)-thiazolidine-dione; 2-thio-3-ethyl-5-(3-methylsulfocarbamylmethyl-2-benzothiazolinyldene)-thiazolidine-dione; 2-thio-3-ethyl-5-(3-methyl-5-phenyl-2-benzoxazolinyldene)-thiazolidine-dione; 2-thio-5-(3'-methyl-2-benzothiazolinyldene)-thiazolidine-dione; 2-thio-5-(3-ethyl-2-benzothiazolinyldene)-thiazolidine-dione; 2,6-dicyclohexyl-3,5-dioxo-4-[2-(3-ethyl-2-benzoxazolinyldene)-ethylidene]-tetrahydro-2H-1,2,6-thiadiazine-1-dioxide; 1-carbethoxy-1-cyano-2-methyl-3-(3-ethyl-2-benzothiazolinyldene)-1-propene; 1,1-dicyano-2-methyl-3-(3-ethyl-2-benzoselenazolinyldene)-1-

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propene; 1,1 - dicyano - 2 - methyl - 3 - (3- ω -sulfo-butyl-2-benzothiazolinyldene)-1-propene;

(7) Complex cyanines, such as: {2-[(3 - ethyl - 4,5-diphenyl - 2 - thiazolinyldene) - methyl] - 3 - allyl-4-oxo - 5 - [1 - phenyl - 2 - (3 - ethyl - 2 - benzothiazolinyldene) - ethylidene]-thiazolinium}-5,5' - bis[2 - thio - 3-ethyl-thiazolidine-dione]-oxonolate.

E. Azenium dyestuffs such as:

Toluylene blue (C.I. 49,140); Flavinduline O (C.I. 50,000); Neutral Red (C.I. 50,040); Induline Scarlet (C.I. 50,080); Phenosafranine (C.I. 50,200); Safranin T (C.I. 50,240); Aniline blue BB (C.I. 50,405) which is used for infrared sensitization; Gallocyanine (C.I. 51,030); Nile blue BB (C.I. 51,185); Basic Blue for leather N 2B (C.I. 51,190); Thionine Ehrlich (C.I. 52,000); Medicinal Methylene blue (C.I. 52,015) which is used for infrared sensitization; Thiocarmine R (C.I. 52,035) which is used for infrared sensitization; Hydrone blue R (C.I. 53,630).

F. Azo-dyestuffs such as:

Janus green B (C.I. 11,050); Interchem Acetate Yellow G (C.I. 11,855); Methyl Orange (C.I. 13,025); Oxanil Yellow GR (C.I. 13,900); Cresol red (C.I. 16,100); Crystal Ponceau 6R (C.I. 16,250); Tartrazine (C.I. 19,140); Congo-red (C.I. 22,120); Congo Corinthe G (C.I. 22,145); Chicago blue 6B (C.I. 24,410); Rouge au Gras B (C.I. 26,105); Chrysophenine G (S. 726).

G. Anthrachinone dyestuffs, such as:

Alizarine (C.I. 58,000); Alizarine Red S (C.I. 58,005); Alizarine Irisol R (C.I. 60,730); Violet Cibacete B marketed by Ciba A.G., Basel, Switzerland; Alizarine cyanid green 5G (C.I. 62,560); Toluidine blue (C.I. 63,340); Alizarine rubinol R (C.I. 68,215).

H. Indigo dyestuffs, such as:

Indigo (C.I. 73,000); Indigotine I (C.I. 73,015); Indigo disulfonate.

I. Vinylene compounds, such as:

Uvitex RBS (C.I. 40,620); 4,4'-bis(p-dimethylamino-benzylidene ammonium)-stilbene-2,2'-disulfobetaine; 4,4'-bis[(4 - amino - 6 - β - hydroxyethylamino - 2 - s - triazinyl)-amino]-stilbene-2,2'-disodium sulfonate.

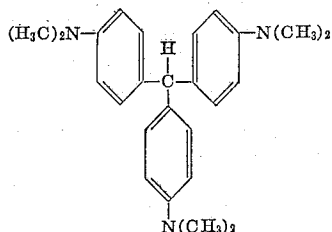
J. Azomethine dyestuffs, such as:

1 - (3 - methyl - 2 - naphtho - (1,2-d) - thiazolinyldene - 2 - p - chlorophenyl-iminobutane; 1-p-nitrophenyl-amino - 3 - p - nitrophenylimino - 1 - propene-hydrochloride; bis - 2 - sulfo - 4 - (p-dimethyl-aminobenzylidene)-amino-benzene; p - dimethylaminobenzaldehyde-thiosemicarbazone; 2-(2,4,6-trioxybenzylidene amino)-diphenylamine.

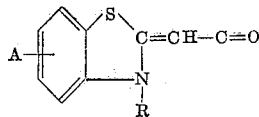
K. Other dyestuffs such as:

Blue (C.I. 74,200); Chlorophyllum (C.I. 75,810); phenol red, and 1-(2,4,6-trinitrophenyl)-1'-(3-methyl-2-benzothiazolinyldene)-propane.

L. Leuco crystal violet according to the formula:



M. Acymethylene derivatives of benzothiazoline of the formula:



wherein

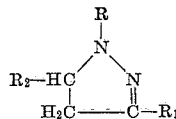
R represents an alkyl group

R₁ represents an alkyl radical or a heterocyclic radical such as 3-pyridyl, and

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A represents a hydrogen atom, an alkyl group or an oxyalkyl group.

N. Pyrazoline derivatives according to the formula:



wherein

R, R₁, R₂ each represent a phenyl group or a p-halophenyl group.

O. Tetrachloro-p-quinone (suited for infra-red sensitization):

The sensitizers are generally coloured compounds mostly colouring the photoconductive layer undesirably. By using acid compounds according to this invention in the presence of certain coloured sensitizers, the intensity of the undesirable colour in the sensitized photoconductive layers decrease and the colour even can disappear.

In the preparation of the recording material according to the invention many techniques may be used for applying the photoconductive layer. The dispersion comprising the photoconductive zinc oxide and the binding agent is uniformly spread over the surface of a suitable backing e.g. by centrifuging, spraying, brushing or coating whereupon the formed layer is dried in such a way that a uniform photoconductive layer is obtained on the surface of the backing. The formed layer is preferably dried rapidly e.g. by a hot air current or by infra-red radiation.

The thickness of the photoconductive layer is not critical but is determined by the requirements of each separate case. In general the thickness of the layer is not less than 5 μ and not more than 30 μ and preferably varies between 5 and 15 μ .

In the preparation of the recording material according to the invention, an electrically conductive element is preferably used as support for the photoconductive layer, such as a plate or sheet, or an insulating plate or sheet provided with an electrically conductive layer. By electrically conductive element is understood a plate, sheet or layer the specific resistivity of which is smaller than that of the photoconductive layer i.e., generally smaller than 10⁹ ohm cm., but preferably smaller than 10⁵ ohm cm.

Suitable conductive plates are e.g. plates of aluminium, zinc, copper, tin, iron.

Suitable conductive sheets are e.g. films made of polymer substances with low specific resistivity such as polyamide films or paper sheets with low specific resistivity. Good results are obtained when using paper sheets comprising hygroscopic and/or antistatic substances as described in Belgian Patent No. 587,301. Preferably, these hygroscopic and/or antistatic substances are incorporated into the material during the paper manufacturing process either by adding them to the paper pulp or by an after-treatment before or after calendering the paper sheets. These substances can likewise be incorporated into the paper sheet by applying to the raw paper stock a composition comprising the hygroscopic and/or the antistatic substances.

In addition to the usual kinds of paper, synthetic kinds of paper can likewise be used such as those described in Belgian Patent No. 587,301.

In addition to the usual kinds of paper, synthetic kinds of paper can likewise be used such as those described in Belgian Patent No. 587,301.

As suitable supports can also be mentioned glass plates provided with a conductive layer e.g. a transparent silver; gold or tin oxide layer e.g. which is applied on the glass plates by means of vacuum vaporization.

Further suitable supports are insulating sheets provided with a conductive layer e.g. a thin metal foil or

a layer containing electrically conductive and/or hygroscopic substances. Such sheets are described in the Belgian Patent No. 587,301.

Photoconductive recording materials according to this invention can be used according to any technique whereby on a photoconductive member a radiation image is registered.

According to one of the most important techniques an electrostatic latent image is formed on a photoconductive member by image-wise applying of an electrical charge or by image-wise carrying off a charge which is present onto a homogeneously electrostatically charged photoconductive member.

If the last mentioned method is used the photoconductive layer can be charged by any of the methods usual in electrophotography e.g. by rubbing with a smooth material or with a material possessing a high electric resistivity e.g. a cylinder coated with polystyrene, by corona discharge, by contact charge or by discharge of a capacitor; after being charged, the photoconductive member is image-wise exposed to a suitable electromagnetic radiation whereby the radiated areas of the photoconductive layer are discharged and an electrophotographic latent image is obtained. The electrostatic latent image is then converted into a visible image either on the photoconductive member itself or on a material to which the electrostatic latent image is first transferred e.g. by applying the method as described in British Patent No. 772,873.

The conversion of the original or transferred latent image into a visible image can be achieved using any of the known techniques in electrophotography wherein use is made of the electrostatic attraction or repulsion of finely divided coloured substances used e.g. in the form of a powder or powder mixture (U.S. Patent No. 2,297,691) in an electrically insulating liquid (e.g. in the form of suspension) (British Patent No. 755,486) or in a gas (e.g. in the form of aerosol), or in the form of finely divided coloured liquid drops present e.g. in an electrically insulating liquid (e.g. in the form of dispersion) or in a gas (e.g. in the form of aerosol). By suitably choosing of the sign of the charge of the developing powder or developing liquid a negative or positive print can be obtained as well from any original.

The original or transferred visible images can, if needed, be fixed according to one of the methods known in electrophotography e.g. by heating or by chemical reaction. They can be transferred onto another support according to a method described in the British Patent No. 658,699, and fixed hereon.

As an alternative to development by techniques generally known in electrophotography, other techniques can also successfully be used. For example a process according to the Belgian Patents Nos. 585,224 and 579,725.

The present invention is not limited in regard to the particular way in which the new photoconductive recording materials are used, and the method of charging the exposure technique, the transfer (if any), the method of developing and the method of fixing as well as the materials used in these steps can be chosen according to requirements.

Photoconductive recording material according to the present invention can be applied in reproduction techniques wherein different kinds of radiations, not only electromagnetic radiations as hereinbefore referred to but also nuclear are used. For this reason it should be pointed out that although materials according to the invention are mainly intended for application in processes involving an exposure, the term "electrophotography" wherever appearing in the description and the claims, is used broadly and comprises both xerography and radiography.

The following examples illustrate the present invention.

Example 1

A suspension of 100 g. of zinc oxide in 330 cm.³ of ethyl alcohol is ground for 2 h. in a ball-mill, which suspension is called suspension A. A same quantity of zinc oxide suspension is treated with 1 cm.³ of monobutylphosphate, which suspension is called suspension B. After adding 330 cm.³ of an 8% solution of copoly (vinyl acetate/vinyl stearate) (85/15) in ethanol to both suspensions as a binding agent, these suspensions are ground once again for 48 h. in a ball-mill. Just before coating, a required amount of Fluorescein (C.I. 45,350) is added as a sensitizer.

The obtained photoconductive compositions are applied onto a baryta coated paper support of 90 g./sq. m. by knife-coating and the obtained layers are dried at 80° C. Their thickness amounts to about 15μ.

Both materials are now stored for 15 h. in a room of 25° C. with a relative humidity of 80%. Thereupon both materials are charged, exposed and developed in a known way. It is stated that the layer formed from suspension B has a higher maximum density and a harder gradation than that formed from suspension A. So the material obtained from suspension B is most suited for reflex-exposure.

On comparing the dark-decay curves of both materials (curves of discharge in the dark vs. time), it is stated that the electrophotographic material, the zinc oxide of which has been treated with acid, carries a charge better than the electrophotographic material, the zinc oxide of which has not been acid-treated.

Example 2

The following mixture is ground for 24 h. in a ball-mill:

Copoly(vinyl acetate/vinyl stearate) (85/15)	g	4
Ethyl alcohol	cm. ³	100
Lead-free zinc oxide	g	15
Monobutyl phosphate	cm. ³	0.4
Bis(carboxymethylene)-disulfide	g	0.1

The obtained suspension is called suspension A. On the other hand, the following mixture is ground for a same time:

Copoly(vinyl acetate/vinyl stearate) (85/15)	g	4
Ethyl alcohol	cm. ³	100
Lead-free zinc oxide	g	15

The obtained suspension is called suspension B. Before coating, 1 part of suspension A is mixed with 3 parts of suspension B. Coating and finishing are carried out according to known processes. A delayed dark-decay is obtained.

Example 3

To 50 cm.³ of a 15% solution in methylene chloride of a copoly[vinyl carbazole/ethyl methacrylate] prepared as described in Belgian patent specification 588,050, a ground dispersion of 15 g. of zinc oxide in 50 cm.³ of ethanol is added.

After adding 0.1 g. of monobutyl phosphate, this suspension is cast onto baryta-coated paper of 70 g./sq. m.

A very good uniformity of the layer is obtained, i.e.: the zinc oxide is very homogeneously divided whereby this layer shows a very uniform covering on the image areas after charging, exposing and developing. When no acid was added, an unsharp image with little blackening and insufficiently bright background is obtained.

Example 4

Two identical dispersions of 30 g. of lead-free zinc oxide in 75 cm.³ of toluene are prepared. To one of these, 1 cm.³ of a 10% monobutyl phosphate solution is added. To the other one no acid is added. Both dispersions are separately ground in a ball-mill for 48 h.

Thereupon 25 cm.³ of a 60% solution of silicone resin in toluene are added to each dispersion and homogeneously mixed therewith. Each of these dispersions is separately applied onto an aluminum foil. After drying, the thickness of the coated layers amounts to 12–13 μ . Now, a latent electrostatic image is obtained on both materials by charging and exposing under the same circumstances. Half the image surface of both materials is developed. The other image half is developed in the same way as the first half after 1 h. of storing in the dark at a relative humidity of 44%. The electrophotographic material containing monobutyl phosphate shows in the last developed image half an image with practically the same covering power and gradation as the image of the first developed image half.

The material containing no monobutyl phosphate shows in the last developed image half an image with insufficient blackening and contrast.

Example 5

A mixture consisting of 100 g. of zinc oxide, 330 cm.³ of acetone and 33 g. of copoly[vinyl chloride/vinyl acetate/vinyl alcohol] (91/3/6) is ground for 48 h. in a ball-mill. To this dispersion 3.3 cm.³ of a 10% solution of monobutyl phosphate in acetone are added. After coating onto a baryta-coated paper support of 60 g./sq. m. the material is dried. The dried layer has a thickness of 15 μ . After charging with a corona apparatus, the material is exposed for 4.5 sec. through a diapositive to a 100 watt lamp placed at a distance of 10 cm. The latent image is developed with a tribo-electrically charged powder consisting of iron powder as a carrier and of a xerographic developing powder. After electrostatically transferring the powder-image and heat-fixing, an image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C. and at a relative humidity of 44%, is 10 times larger than that of the charged material in the same way but containing no acid.

Example 6

A mixture consisting of 100 g. of zinc oxide, 660 cm.³ of methylene chloride and 26 g. of polystyrene and to which 6.6 cm.³ of a 10% solution of monobutyl phosphate in methylene chloride are added, is ground for 48 h. in a ball-mill.

After coating onto a baryta-coated paper of 60 g./sq. m. the material is dried. The layer has a thickness of 18 μ . Charging, exposure, development and fixing are carried out as in Example 5. An image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C. and at a relative humidity of 44%, is 3 times larger than that of the material charged in the same way but containing no acid.

Example 7

A mixture consisting of 100 g. of zinc oxide, 500 cm.³ of ethanol and 10 g. of a butyraldehyde acetal of polyvinyl alcohol and to which 5 cm.³ of a 10% solution of monobutyl phosphate in ethanol are added, is ground for 48 h. in a ball-mill.

After coating onto a baryta-coated paper of 60 g./sq. m., the material is dried. The layer has a thickness of 10 μ . Charging, exposure, development and fixing are carried out as in Example 5. An image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C. and at a relative humidity of 44%, is 6.5 times larger than that of the material charged in the same way but containing no acid.

Example 8

A mixture consisting of 100 g. of zinc oxide, 660 cm.³ of methylene chloride and 50 g. of copoly[N-vinyl carbazole/ethyl acrylate] (74.5/25.5) prepared as described in Belgian Patent No. 588,050, and to which 6.6 cm.³ of a 10% solution of monobutyl phosphate in methylene chloride are added, is ground for 48 h. in a ball-mill.

After casting onto a baryta-coated paper of 60 g./sq. m., the material is dried. The layer has a thickness of 15 μ . Charging, exposure, development and fixing are carried out as in Example 5. An image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C. and at a relative humidity of 44% is 5 times larger than that of the material charged in the same way but containing no acid.

Example 9

A mixture consisting of 100 g. of zinc oxide, 500 cm.³ of methylene chloride and 10 g. of a polycarbonate of 2,2-bis(4-hydroxyphenyl)-propane and to which 5 cm.³ of a 10% solution of monobutyl phosphate in methylene chloride are added, is ground for 48 h. in a ball-mill.

After coating onto a baryta-coated paper of 60 g./sq. m., the material is dried. The layer has a thickness of 15 μ . Charging, exposure, development and fixing are carried out as in Example 5. An image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C., and at a relative humidity of 44% is 8 times larger than that of the material charged in the same way but containing no acid.

Example 10

A mixture consisting of 100 g. of zinc oxide, 500 cm.³ of methylene chloride and 50 g. of the polyester of 2,2-bis(4-hydroxyphenyl)-propane with fumaric acid, prepared as described in Belgian Patent No. 563,173, and to which 5 cm.³ of a 10% solution of monobutyl phosphate in methylene chloride are added, is ground for 48 h. in a ball-mill.

After casting onto a baryta-coated paper of 60 g./sq. m., the material is dried. The layer has a thickness of 15 μ . Charging, exposure, development and fixing are carried out as in Example 5. An image with an excellent covering power and specially good contrast is obtained. These characteristics are still present when finishing in circumstances of high relative humidity.

The relaxation time of the charged material with the above-mentioned composition, measured in the dark at 20° C. and at a relative humidity of 44%, is 4 times larger than that of the material charged in the same way but containing no acid.

Example 11

300 g. of zinc oxide in 3 l. of water are ground in a ball-mill for 24 h. To this dispersion are then slowly added with stirring 30 cm.³ of a 10% solution of monobutyl phosphate in ethanol. Thereupon 180 cm.³ of a 55% aqueous dispersion of polyvinyl acetate are added to the treated zinc oxide dispersion. Then 9 cm.³ of a 1% solution of Rose Bengale (C.I. 45,435 and C.I. 45,440) in ethanol are added to the dispersion as a sensitizer.

The photoconductive zinc oxide dispersion is coated onto a baryta-coated paper support of 90 g./sq. m. according to the knife-coating system. After drying, the electrophotographic material is charged with a corona, exposed through a transparency and developed with a carrier-toner developing powder consisting of iron filings and a powdery mixture of fusible resin and carbon dust. The image is fixed by heat. A contrasty image is obtained with a good covering power.

Example 12

1500 g. of zinc oxide in 5 l. of a 4% solution of copoly-(vinyl acetate/vinyl stearate) (85/15) in ethanol are ground for 24 h. in a ball-mill. 500 cm.³ of this dispersion are diluted by adding 500 cm.³ of a 4% solution of copoly(vinyl acetate/vinyl stearate) (85/15) in ethanol. To this diluted dispersion, a 1% solution of Fluoresceine Sodium (C.I. 45,350) in ethanol are added. Thereupon 60 g. of zinc isopropyl phosphate are added and the mixture is stirred for 2 h.

After grinding, the dispersion is dip-coated onto a baryta-coated paper support and then dried by infra-red radiation.

The dried photoconductive material is then stored for some hours at 20° C. and 80% of relative humidity. Hereupon, the photoconductive material is negatively charged and exposed through a transparency. The latent electrostatic image is developed with a powdery mixture of fusible resin and carbon dust. An image with a very good covering power is obtained.

On a same material containing, however, no zinc isopropyl phosphate, a very faint image is obtained.

If zinc isopropyl phosphate is replaced by zinc phenyl phosphate the same good results are obtained.

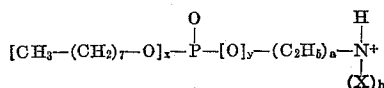
Example 13

1500 g. of zinc oxide in 3 l. of methanol, wherein 120 g. of copoly(vinyl acetate/vinyl laurate) (80/20) are dissolved, is ground in a ball-mill for 24 h. After grinding, the dispersion is diluted with 2 l. of a solution of 800 g. of copoly(vinyl acetate/vinyl laurate) (80/20) in methanol.

The obtained dispersion is divided into parts of 50 cm.³ and to each part 50 cm.³ of a 4% solution of copoly-(vinyl acetate/vinyl laurate) (80/20) in methanol are added.

To each part of dispersion, an amount of a 10% ethanol solution of a phosphorous compound as listed hereinafter is added with strongly stirring:

An acid phosphate neutralized with an amine



wherein

$x=1$ or 2 ,

$y=3-x$,

$a=1, 2$ or 3 ,

$b=3-a$,

$\text{X}=\text{hydrogen}$ or ethoxyl .

	Cm. ³
Octyl acid phosphate	1
Phytic acid	1
Diethyl phosphite	1
Di-n-butyl acid pyrophosphate	1
Mono-methyl acid orthophosphate	1
Ethyl-lauryl acid orthophosphate	1.5
Mono-di-(2-ethyl hexyl) acid orthophosphate	1.5
Phenyl acid phosphate	0.6
Mono-n-butyl acid orthophosphate	1.5

Finally, to each part of dispersion of 0.4 cm.³ of a 1% solution of Rose Bengale (C.I. 45,435 and C.I. 45,440) in ethanol is added as an optical sensitizer.

By dip-coating, each part of dispersion is applied onto a baryta-coated paper support in such a way that each layer covers 12 sq. m. of paper.

After drying the electrophotographic material is stored at 22° C. and 75% of relative humidity. After charging with a negative corona and exposure through a transparency, the obtained latent image is developed with a carrier-toner powder.

Very contrasty images are obtained, which is not the case when none of the above phosphorous compounds is added to the photoconductive layer.

On comparing the dark-decay curves measured at 20° C. and 50% of relative humidity, of a material containing one of the above phosphorous compounds and of a material without such a compound, it is seen that the former material carries a charge much longer in the dark than the latter; it thus possesses a larger relaxation time at a higher relative humidity.

Example 14

Example 13 is repeated substituting, however, copoly (vinyl acetate/vinyl stearate) (85/15) for copoly(vinyl acetate/vinyl laurate) (80/20) and ethanol for methanol.

The respectively added amounts of phosphorous compounds are the following:

	Cm. ³
An acid phosphate neutralized with an amine	2
Benzene phosphonic acid	2
Octyl acid phosphate	1.5
Di-n-butyl acid pyrophosphate marketed by Victor Chemical Works, Chicago, Ill., U.S.A.	1.5
Mono-methyl acid orthophosphate	1
Mono-di-(2-ethylhexyl) acid orthophosphate	1.5
Phenyl acid phosphate	2
Mono-n-butyl acid orthophosphate	1

As in Example 13 very contrasty images are obtained.

On comparing the dark-decay curves measured at 20° C. and 50% of relative humidity, of a material containing one of the above phosphorous compounds and of a material without such a phosphorous compound it is seen that the former material possesses a longer relaxation-time than the latter it thus possesses a good dark-resistivity and a good resistance to moisture.

Example 15

1500 g. of zinc oxide in a solution of 120 g. of copoly (vinyl acetate/vinyl stearate) (85/15) in 3 l. of ethanol are ground in a ball-mill for 24 h. This dispersion is diluted with a solution of 800 g. of copoly(vinyl acetate/vinyl stearate) (85/15) in 2 l. of methanol. This diluted dispersion is divided into parts of 50 cm.³ and to each part, 50 cm.³ of a 4% solution of copoly(vinyl acetate/vinyl stearate) (85/15) in ethanol are added.

To each part of dispersion one of the following phosphorous compounds is added with strongly stirring in an amount given hereinafter in percent by weight of zinc oxide.

Zinc butyl phosphate	0.6-10
Copper (II) butyl phosphate	0.6-3
Silver butyl phosphate	0.6-10
Diammonium butyl phosphate	0.6-10
Cobalt butyl phosphate	0.6-10
Barium butyl phosphate	0.6-10

Finally 0.4 cm.³ of a 1% solution of Rose Bengale (C.I. 45,435 and C.I. 45,440) in ethanol is added to each part of dispersion. Each part is then ground once again for 4 h.

The various dispersions are then applied by knife-coating onto a baryta-coated paper support of 90 g./sq. m. After drying, the different samples are tested on their resistance to moisture. The dark-decay curves of these materials measured at 22° C. and 50% of relative humidity show larger relaxation times than the materials containing no phosphates.

Example 16

To 500 cm.³ of a 4% solution of copoly(vinyl acetate/vinyl stearate) (85/15) in ethanol, 225 g. of photoconductive zinc oxide are added. The mixture is ground in a ball-mill for 48 h., whereupon the following composition is added whilst thoroughly stirring:

	Cm. ³
2% solution of copoly(vinyl acetate/vinyl stearate) (85/15) in ethanol	500
10% solution of monobutyl phosphate in ethanol	10
10% solution of succinic acid in dimethyl formamide	10
1% solution of fluoresceine (C.I. 45,350) in ethanol	10

This photoconductive dispersion is applied by knife-coating onto a paper support provided with an aluminum foil at a rate of 10 sq. m. per liter, and dried.

The obtained photoconductive layer is charged till -300 v./cm. by corona apparatus with a tension of -7000 v. at the wires. After exposure and development, a very contrasty image is obtained.

On comparing the dark-decay curves measured at 20° C. and 50% of relative humidity of this material and of a material not containing the above acidic compounds, it is seen that the former material carries a charge a longer time in the dark than the latter, it thus possesses a larger relaxation-time at a higher relative humidity.

Example 17

After thoroughly grinding, the following composition is cast onto a paper support:

Copoly(vinyl acetate/vinyl stearate) (85/15)	--g--	4
Ethyl alcohol	-----cm. ³ --	100
Lead-free zinc oxide	-----g--	15

Onto a part of the obtained material, a second layer is applied by dip-coating it in a 0.4% alcoholic solution of an acid phosphate neutralized with an amine.

Both materials are then stored for 24 h. at room temperature and at a relative humidity of 50%. Charging, exposing and developing is carried out in the same atmospheric conditions. An image obtained on the first material has a higher maximum density than an image obtained on the same material but to which no amine salt of an acid phosphate has been added.

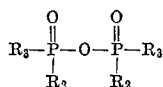
The relaxation time of the former material, measured in the same atmospheric conditions, is much better than that of the latter material.

We claim:

1. Recording material comprising a photoconductive member containing photoconductive zinc oxide dispersed in a binding agent, wherein at least a portion of said zinc oxide is in contact with at least one organic phosphorus compound of the group consisting of:



and

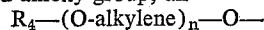


wherein:

R₁ is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group, a halogen atom, and an M—O— group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, and an onium group;

R₂ is a member selected from the group consisting of a halogen atom; an M—O— group wherein M is a member selected from the group consisting of a

hydrogen atom, a metal atom, an onium group; an alkyl group; a substituted alkyl group; an aryl group; a substituted aryl group; an alkoxy group; a substituted alkoxy group; an



radical, wherein R₄ is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group and an acyl group, and *n* represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group and an acyl amino group, and

R₃ is a member selected from the group consisting of an alkyl radical; a substituted alkyl radical; a phenyl radical; an alkoxy radical; a substituted alkoxy radical; an R₄—(O-alkylene)_n—O— radical, wherein R₄ is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group, and an acyl group, and *n* represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group, and an acyl amino group.

2. Recording material according to claim 1, wherein a compound selected from the class consisting of unsubstituted aliphatic mono- and polycarboxylic acids and their anhydrides, containing no more than 10 carbon atoms in a straight chain, and aliphatic mono- and polycarboxylic acids which are substituted by water-solubilizing groups is incorporated in the photoconductive member.

3. Recording material according to claim 1, wherein the photoconductive member is a layer applied to an electrically conductive support.

4. Recording material according to claim 1, wherein the photoconductive member is a layer applied to a paper support.

5. Recording material according to claim 1, wherein said photoconductive member is a photoconductive layer at least 50% of which consists of photoconductive zinc oxide.

6. Recording material according to claim 1, wherein said compound in contact with said zinc oxide is present in an amount of between 0.1 and 10% based on the weight of said photoconductive zinc oxide.

7. Recording material according to claim 1, wherein the weight ratio of zinc oxide to binding agent is between 7:3 and 9:1.

8. Recording material according to claim 1, wherein said binding agent is a copolymer of vinyl acetate and an ester of vinyl alcohol and a higher aliphatic carboxylic acid.

9. Recording material according to claim 8, wherein said organic phosphorus compound is incorporated in said photoconductive layer in an amount between 0.1 and 3% based on the weight of said photoconductive zinc oxide.

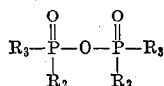
10. Recording material according to claim 9, wherein an aliphatic dicarboxylic acid is incorporated in said photo-conductive layer in an amount between 0.1 and 3% based on the weight of the zinc oxide.

11. Recording material according to claim 1, wherein said organic phosphorus compound is monobutylphosphate.

12. In a recording process the step of exposing to electromagnetic radiation a photoconductive member comprising photoconductive zinc oxide the dark resistivity of which is increased by bringing said photoconductive zinc oxide into contact with at least one organic phosphorus compound of the group consisting of:



and



wherein

R_1 is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group, a halogen atom, and an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, and an onium group;

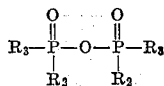
R_2 is a member selected from the group consisting of a halogen atom; an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group; an alkyl group; a substituted alkyl group; an aryl group; a substituted aryl group; an alkoxy group; a substituted alkoxy group; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group and an acyl group, and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group and an acyl amino group, and

R_3 is a member selected from the group consisting of an alkyl radical; a substituted alkyl radical; a phenyl radical; an alkoxy radical; a substituted alkoxy radical; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group, and an acyl group, and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; a substituted amino group; a dialkyl amino group, and an acyl amino group.

13. In a recording process the step of exposing to electromagnetic radiation a photoconductive member comprising photoconductive zinc oxide the dark-resistivity of which is increased by bringing said photoconductive zinc oxide into contact with a compound selected from the class consisting of unsubstituted aliphatic mono- and polycarboxylic acids and their anhydrides containing no more than 10 carbon atoms in a straight chain in combination with at least one organic phosphorus compound of the group consisting of:



and



wherein:

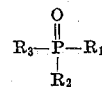
R_1 is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group, a halogen atom, and an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, and an onium group;

R_2 is a member selected from the group consisting of a halogen atom; an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group; an alkyl group; a substituted alkyl group; an aryl group; a substituted aryl group; an alkoxy group; a substituted alkoxy group; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the

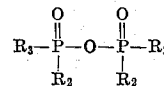
group consisting of an alkyl radical, an alkaryl radical, an amide group and an acyl group, and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group and an acyl amino group, and

R_3 is a member selected from the group consisting of an alkyl radical; a substituted alkyl radical; a phenyl radical; an alkoxy radical; a substituted alkoxy radical; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group, and an acyl group, and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group, and an acyl amino group.

14. In a recording process the step of exposing to electromagnetic radiation a photoconductive member comprising photoconductive zinc oxide the dark-resistivity of which is increased by bringing said photoconductive zinc oxide into contact with a compound selected from the class consisting of aliphatic mono- and polycarboxylic acids which are substituted by water-solubilizing groups in combination with at least one organic phosphorus compound of the group consisting of:



and



wherein:

R_1 is a member selected from the group consisting of a hydrogen atom, a metal atom, an onium group, a halogen atom, and an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom, a metal atom, and an onium group;

R_2 is a member selected from the group consisting of a halogen atom; an $\text{M}-\text{O}-$ group wherein M is a member selected from the group consisting of a hydrogen atom; a metal atom, an onium group; an alkyl group; a substituted alkyl group; an aryl group; a substituted aryl group; an alkoxy group; a substituted alkoxy group; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group and an acyl group, and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group and an acyl amino group, and

R_3 is a member selected from the group consisting of an alkyl radical; a substituted alkyl radical; a phenyl radical; an alkoxy radical; a substituted alkoxy radical; an $\text{R}_4-(\text{O-alkylene})_n-\text{O}-$ radical, wherein R_4 is a member selected from the group consisting of an alkyl radical, an alkaryl radical, an amide group, and an acyl group; and n represents an integer of between 1 and 50; an aryloxy group; a substituted aryloxy group; an ester group; an amino group; a substituted amino group; a dialkyl amino group, and an acyl amino group.

15. In a process according to claim 12, said photoconductive zinc oxide is brought into contact with from 0.1 to 5% of said compound based on the weight of the zinc oxide.

16. In a process according to claim 15, said photoconductive zinc oxide is brought into contact with said phosphorus compound by adding said compound to a

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dispersion of said photoconductive zinc oxide in a solution of a binding agent.

17. In a process according to claim 16, said binding agent is a copolymer of vinyl acetate and an ester of vinyl alcohol and a higher aliphatic carboxylic acid.

18. In a process according to claim 16, said phosphorus compound is added to said dispersion in combination with

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a dicarboxylic acid, the latter being in an amount between 0.1 and 1% based on the weight of the photoconductive zinc oxide.

No references cited.

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