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(54) **Improved photosensitive recording material and a method of recording information by exposure of said material to information-wise modulated activating ultra-violet and/or visible light.**

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DE - A - 2 719 023
FR - A - 2 159 287
FR - A - 2 183 899
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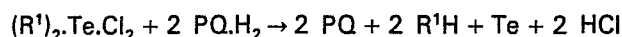
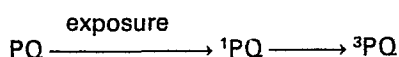
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Improved photosensitive recording material and a method of recording information by exposure of said material to information-wise modulated activating ultra-violet and/or visible light.

The present invention relates to improved photosensitive recording material and a method of recording information by exposure of said material to information-wise ultra-violet and/or visible light.

In the published German Patent Application (DE-A 2,436,132 a process for producing a record of retrievable information has been described in which a recording layer containing as imaging substance an organo-tellurium compound is used. In this process the organo-tellurium compound, which contains halogen, preferably chlorine, linked directly to a tellurium atom and which contains at least one organic substituent comprising a carbonyl group, is reduced image-wise by means of a photo-exposed photo-reductant e.g. a polynuclear quinone. The formation of the tellurium image proceeds by thermal development e.g. by overall-heating the photoexposed material in the range of 80 to 200°C.

The following reaction scheme illustrates said process in which a tellurium metal image is formed:



wherein:

PQ is a photoreductant e.g. phenanthrenequinone,

${}^1\text{PQ}$ is the first excited singlet of said quinone,

${}^3\text{PQ}$ is the triplet state of said quinone,

RH is a hydrogen donor e.g. an organic hydroxy compound,

PQ.H₂ is the photoreductant in reduced state, and

$(\text{R}^1)_2\text{Te.Cl}_2$ is a reducible organo-tellurium compound wherein R¹ is e.g. (C₆H₅COCH₂).

A disadvantage associated with recording materials containing these compounds is their rather low photo-sensitivity.

It has been established experimentally that the exposure energy required for a certain maximum optical density can be lowered considerably by using a recording material containing on the recording layer a blocking layer or sheet that counteracts the penetration of vapour or gas into and the escape of vapours or gases from the recording layer during the thermal development.

In accordance with the present invention a recording material is provided which contains on a support a recording layer containing in admixture in a binder medium:

(1) an organo-tellurium compound containing directly linked to the tellurium atom halogen and at least one organic substituent comprising at least one carbonyl group.

(2) a photoreductant,

(3) a hydrogen-donating compound from which hydrogen can be abstracted by the photo-exposed photoreductant, and is characterized in the one or more blocking layers or a blocking sheet is permanently united with said recording layer, directly or through the intermediary of one or more subbing layers, to counteract the penetration of vapour or gas into and the escape of vapour or gas from the recording layer during thermal development after information-wise exposure to ultra-violet and/or visible light of the material, the support and/or said blocking layers or blocking sheet being transparent to said light.

The gas or vapour impermeability of said layer or sheet is preferably such that when the recording layer of the control material A—O described in the present Example 1 is coated with said layer or sheet the described information-wise exposure and thermal development of the coated material yields tellurium images of which the image in the coated material has a maximum optical density (D) at least 0.2 higher than the corresponding maximum optical density of a tellurium image formed under identical exposure and processing conditions in an identical material but not coated with said layer or sheet.

A blocking layer or sheet may be produced from polymeric materials, which include natural, modified natural, and synthetic resins. Examples are cellulose esters such as cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, polystyrene, polyvinyl acetate, polyvinyl chloride, silicone resins, poly(acrylic ester) and poly(methacrylic ester) resins and fluorinated hydrocarbon resins, and mixtures of the foregoing materials. Specific examples of various useful synthetic polymeric materials prepared by addition polymerization include: poly(n-butyl methacrylate), poly(isobutyl methacrylate), copolymers of vinylidene fluoride and trifluorochloroethylene, a polyvinyl-n-butylal, a copoly(vinyl acetate/vinyl chloride), a copoly(acrylonitrile/butadiene/styrene), a copoly(vinyl chloride/vinyl acetate/vinyl alcohol) and poly(N-methoxymethyl acrylamide).

Apart from the polymers produced by addition polymerization of unsaturated monomers, likewise

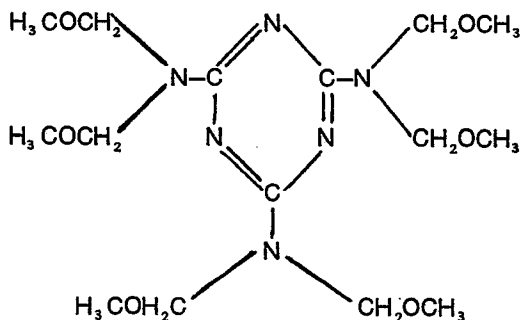
polymers prepared by polycondensation, e.g. polyurethanes polyamides and polyester resins, may be used for preparing a useful blocking layer or sheet for the recording material of the present invention.

According to a specific embodiment a blocking layer of the recording material according to the present invention is made of a cross-linked polymer mass obtained by an acid-catalyzed reaction of a polymer or mixture of polymers containing reactive hydrogen atoms e.g. forming part of one or more groups of the class consisting of free hydroxyl groups, —NHCO—O— groups, and —COOH groups, and an organic compound containing a plurality of etherified N-methylol groups, preferably $\text{—N—CH}_2\text{OCH}_3$ groups as cross-linking agent.

A polymer containing reactive hydrogen atoms forming part of free hydroxyl groups and appropriate for acid-catalyzed cross-linking with compounds containing etherified N-methylol groups is, e.g., a polyester comprising free hydroxyl groups, a polyvinyl acetal in which some of the hydroxyl groups of the polyvinyl alcohol starting product have not been acetalized, a copolymer of vinyl alcohol and vinyl chloride, or a copolymer of vinyl chloride, vinyl acetate and vinyl alcohol. A preferably used polymer containing free hydroxyl groups is a polyvinyl butyral with from 80 to 90% by weight of vinyl butyral units, 7 to 20% by weight of vinyl alcohol units and 0 to 3% by weight of vinyl ester units, e.g. vinyl acetate units. The molecular weight of the polyvinyl butyral may be within a broad range but is preferably between 45,000 and 55,000. Polyvinyl butyrals characterized by an intrinsic viscosity of 0.75 to 1.25 dl.g^{-1} determined in ethanol at 20°C are particularly useful.

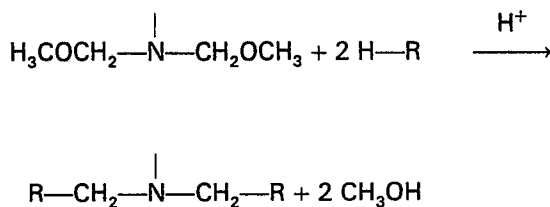
Polymers containing reactive hydrogen atoms forming part of —NH—CO—O— groups and appropriate for acid-catalyzed cross-linking with compounds containing etherified N-methylol groups are polyurethane polymers e.g. as described in United States Patent Specification 3,743,833. An example of a useful polyurethane polymer that is commercially available is sold under the trade-name ESTANE 5707 F—1 (ESTANE is a trademark of the B.F. Goodrich Chemical Company, Cleveland, Ohio, USA, for a polyurethane resin).

Appropriate crosslinking agents containing a plurality of etherified N-methylol groups are derived from reaction products of formaldehyde with urea or with melamine. A particularly useful crosslinking compound for use in combination with said polyvinyl butyral is hexakis(methoxymethyl)-melamine corresponding to the following structural formula:



Such compound is commercially available under the trade name CYMEL 300 of American Cyanamid Company, New York, USA.

It is assumed that the acid-catalyzed cross-linking reaction of said compound with a polymer having reactive hydrogen atoms takes place as follows:



wherein R represents the organic group of the polymer.

The reaction proceeds preferably at elevated temperature. A preferred cross-linking temperature also called curing temperature is in the range of 80 to 160°C.

The amount of cross-linking agent with respect to said cross-linkable polymer(s) is preferably in the range of 5 to 20% by weight.

In practice it is preferred to use as catalyst strong acids such as hydrochloric acid, phosphoric acid, monobutyl phosphate, polystyrene sulphonic acid and p-toluene sulphonic acid. Preferably p-toluene sulphonic acid is used which is an acid that is soluble in an organic solvent such as ethanol in

which the cross-linkable polymer e.g. the polyvinyl butyral can be dissolved. The amount of acid catalyst with respect to cross-linkable polymer is preferably in the range of 0.2 to 4% by weight. Since as is apparent from the reaction scheme hereinbefore hydrochloric acid is formed during thermal development it is possible to effect cross-linking in situ during thermal development. The thickness in dry state of the blocking layer in the form of a coating on the recording layer is preferably at least 5 μm e.g. in the range of 5 to 200 μm . The blocking layer will generally be an outermost coating. However, recording materials wherein such coating is itself overcoated are not excluded from the scope of the invention.

The blocking coating may be applied from a polymer solution or dispersion, e.g. a latex which after drying and evaporation of the solvent or liquid dispersing medium leaves a continuous polymer layer. Care should be taken to apply the polymer solution or dispersion from a liquid medium that does not dissolve or does not give rise to swelling of the binder of the recording layer. A suitable blocking layer may likewise be applied in the form of a sheet by lamination. An adhesive layer is normally used to more firmly bind such coating to the recording layer. Adhesives and compositions for producing protective laminates are described, e.g. in the United States Patent Specification 3,164,719 of Herbert Bauer, issued January 5, 1965.

According to a simple embodiment a commercially available pressure-sensitive adhesive sheet is used to obtain the desired blocking of the recording layer. Blocking sheets applied by means of an adhesive to the recording material and that are useful for the purpose of the present invention may have a thickness in the range of 50 to 200 μm .

According to still another embodiment a layer of polymerisable monomers is applied and allowed to polymerize in situ on the recording layer. A monomer suited for forming a blocking layer in that way is acrylamide.

Reducible organo-tellurium compounds (1) that are particularly suitable for use in a recording material of the present invention correspond to the following general formula:



wherein:

R represents an organic group, which is linked by a carbon atom to the tellurium atom and contains at least one carbonyl group,
x is 1, 2 or 3, and
x + y = 4.

Such compounds as well as their preparation are described in the published German Patent Application (DT-OS) 2,436,132.

A preferred class of imaging agents are organo-tellurium compounds corresponding to the following general formula:



wherein:

Ar stands for an aromatic group including a substituted aromatic group e.g. phenyl, methoxyphenyl, tolyl or naphthyl.

Bis(phenacyl)-tellurium dichloride is a preferred imaging agent for use according to the present invention in combination with a photoreductant, a hydrogen-donor and optionally at least one acid-sensitive reducing agent precursor.

Any compound that obtains reducing power with respect to said tellurium compound through photo-induced hydrogen abstraction from a hydrogen-donating compound (3) can be used as photoreductant (2).

A survey of photoreductants is given in Research Disclosure October 1974, p. 14—17, No. 12617.

Photoreductants (2) preferred for use according to the present invention are aromatic diketones and especially 1,2- and 1,4-benzoquinones with at least one fused-on carbocyclic aromatic ring.

Examples of photoreductants are listed in the following table 1 together with their approximate spectral sensitivity range.

TABLE 1

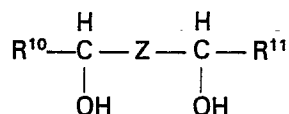
Photoreductant	Spectral sensitivity range (nm)
9,10-phenanthrenequinone	200 — 400 — 500 U.V. visible
1,1'-dibenzoylferrocene	400 — 600
1-phenyl-1,2-propanedione	400 — 500
2-hydroxy-1,4-naphthoquinone	400 — 500
benzil	400 — 450
furil	400 — 480
diacetylferrocene	400 — 450
acetylferrocene	400 — 450
1,4-bis(phenyl glyoxal)-benzene	400 — 500
o-naphthoquinone	up to about 560

The following are illustrative photoreductants that are sensitive in the range up to about 400 nm, and, therefore, are useful only in the ultraviolet range: benzophenone; acetophone; 1,5-diphenyl-1,3,5-pentanetrione; ninhydrin 4,4'-dibromobenzophenone; 2-t-butylanthraquinone and 1,8-dichloro-anthraquinone.

In the reduction of said organo-tellurium compounds 9,10-phenanthrenequinone and 2-t-butyl-anthraquinone are especially satisfactory.

The hydrogen-donating compound (3) is any conventional source of labile hydrogen as described e.g. in the United States Patent Specification 3,881,930. Herein especially hydrogen-donating compounds are described, which have a hydrogen atom bonded to a carbon atom to which is also bonded the oxygen atom of a hydroxy group and/or the trivalent nitrogen atom of an amine substituent.

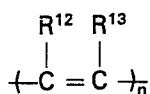
Preferred hydrogen-donating compounds (3), from which hydrogen can be abstracted by said photo-exposed photo-reductant correspond to the following general formula:



wherein:

each of R^{10} and R^{11} , which may be the same or different, represents hydrogen, a hydrocarbon group including a straight chain, branched chain, and cyclic hydrocarbon group, which groups may be substituted, e.g. an alkyl group, a hydroxyalkyl group, a cycloalkyl group or an aryl group, or an alkoxy-carbonyl group e.g. a $\text{C}_2\text{H}_5-\text{O}-\text{CO}-$ group,

Z represents a single bond, an ethylene group $-(\text{C} \equiv \text{C})_n-$ or the group



wherein n represents a whole number e.g. 1 and 2, and each of R^{12} and R^{13} , which may be the same or

different, represents hydrogen, or an alkyl group e.g. methyl or together form part of a carbocyclic or heterocyclic ring e.g. phenylene ring.

Specific examples of such hydrogen-donating compounds are listed in the following table 2 and can be found in the published German Patent Application DE-A 2719023.

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TABLE 2

10	No. of the compound	R^{10}	Z	R^{11}	Boiling point (BP) °C or Melting point (MP) °C
	1	H	—	H	BP 198
15	2		—	H	MP 67
	3	H_3C-	—	H	BP 189
20	4	H_3C-	—	$-CH_3$	BP 183
	5	H	$-C \equiv C-$	H	MP 52–54
25	6	H		H	MP 112
	7	$HO(CH_2)_4-$	—	H	BP 178/5 mm Hg
30	8	C_2H_5OCO-	—	C_2H_5O-CO-	BP 280

The preparation of these compounds is known to those skilled in the art. A particularly suitable hydrogen-donating compound is phenyl-1,2-ethanediol (compound 2 of table 2).

In addition to the above reagents (1) to (3) an organic reducing agent precursor may be used, which according to the published German Patent Application DE-A 2802666 increases the photographic speed of the recording material. From said organic reducing agent precursor by the action of an acid, e.g. HCl formed in the imaging reaction, a reductor is set free image-wise, whereby image-wise reduction of the organo-tellurium compound takes place. When an acid sensitive organic reducing agent precursor is used it is not recommended to use simultaneously a covering layer that contains non-differentially an acid for effecting overall curing or crosslinking of that layer since some of that acid could reach the recording layer and set free the reductor all over the recording layer and reduce the tellurium compound in a non-differential way giving rise to background fog.

A class of organic reducing agent precursors, from which by the action of an acid a reducing agent for said organo-tellurium compound can be set free includes para and ortho-dihydroxy aryl compounds of which at least one of the hydroxyl groups has been esterified and of which the remaining hydroxyl group (if any) may have been etherified. By acid-catalyzed hydrolysis the hydroxyl group can be obtained in free state again so that the compound involved regains its reducing properties.

Another class of acid-sensitive organic reducing agent precursors is derived from pyrazolidin-3-one reductors, in which the active hydrogen atom in 2-position is temporarily blocked e.g. by reaction with an isocyanate or an acid halide.

Representatives of both classes of reducing agent precursors are listed in the following table 3.

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TABLE 3

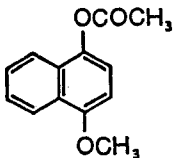
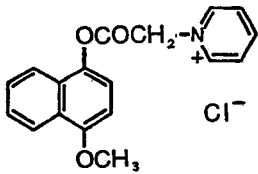
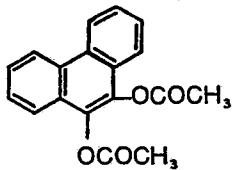
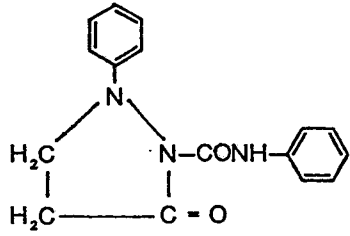
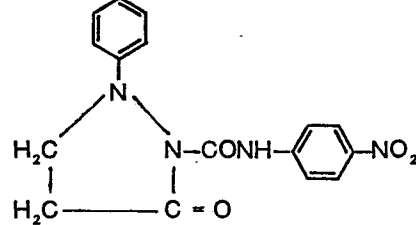
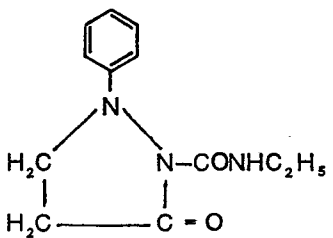
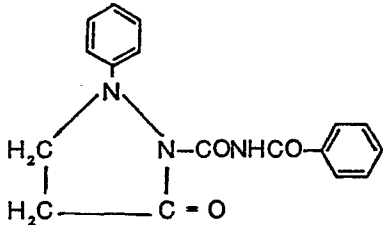
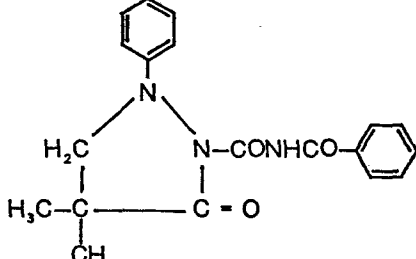
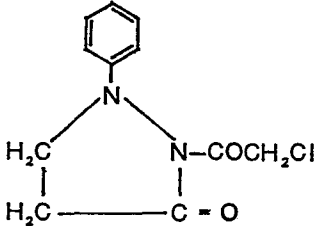
5	Compound No.	Chemical Structure	Melting point (MP) or Boiling point (BP) °C
10	1		BP 140–144 (0,05 mm Hg)
20	2		MP about 200
30	3		MP about 200
40	4		MP 132
50	5		MP 181
60	6		MP 135

TABLE 3 (Continued)

Compound No.	Chemical Structure	Melting point (MP) or Boiling point (BP) °C
7		MP 182
8		MP 164
9		MP 97

The preparation of these compounds is described in said published German Patent DE—A 2802666.

Particularly suitable binders for use in recording layers of the present invention are organic polymeric materials.

Illustrative thereof are cyano-ethylated starches, celluloses and amyloses having a degree of substitution of cyano-ethylation of at least 2; polyvinylbenzophenone; polyvinylidene chloride; polyethylene terephthalate; cellulose-esters and ethers such as cellulose acetate, cellulose propionate, cellulose butyrate, methylcellulose, ethylcellulose, hydroxypropylcellulose, polyvinylcarbazole, polyvinyl chloride; polyvinyl methyl ketone, polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl methyl ether, polyacrylic and polymethacrylic alkyl esters such as polymethyl methacrylate and polyethyl methacrylate; copolymer of polyvinyl methyl ether and maleic anhydride; various grades of polyvinyl formal resins such as so-called 12/85, 6/95 E, 15/95 S, 15/95 E, B-79, B-98, and the like, sold under the trademark "FORMVAR" — of Monsanto Company, St. Louis, Mo., USA.

Of special utility is polyvinyl formal 15/95 E, which is a white, free-flowing powder having a molecular weight in the range of 24,000 — 40,000 and a formal content expressed as % polyvinyl formal of approximately 82%, possessing high thermal stability, and excellent mechanical durability.

A dry photographic coating containing the above-mentioned ingredients can be formed by dissolving the binding agent or mixture of binding agents in a suitable inert solvent, which acts as dispersing or dissolving medium for the other ingredients and which is removed from the coating composition by evaporation so that a solid photographic recording layer on a properly chosen support is left. The supports may be of a kind encountered in silver halide photographic materials, e.g. paper and resin film.

The photoreductant is used in the recording material in an amount which is preferably at least equimolar with respect to the organo-tellurium compound. The coverage of the organo-tellurium compound is preferably in the range of 1 to 10 g per sq. m. The amount of hydrogen-donating compound is preferably at least 50% by weight with respect to the organo-tellurium compound.

The amount of acid-sensitive reducing agent precursor is not critical. Large improvements in

sensitivity are obtained with amounts between 50 to 100% by weight with respect to the organo-tellurium compound.

The present invention includes a recording method in which the above defined recording material is used. Said method includes the steps of information-wise exposing said material to ultra-violet and/or visible light to which the photo-reductant is sensitive and overall heating to develop a tellurium image in the recording material.

An information-wise ultraviolet exposure is normally used in combination with an aromatic diketone as photo-reductant.

The heat-development preferably proceeds in the temperature range of 80°C to 200°C and in general lasts approximately 30 s to 300 s depending on the temperature.

The heat required to produce the tellurium metal image can be supplied in various ways. So, the recording material can be developed by heat transport from hot bodies e.g. plates or rollers or by contact with a warm gas stream e.g. hot air. Furthermore, the metal image can be formed by means of infrared radiation.

The following examples illustrate the present invention without, however, limiting it thereto. All percentages or ratios are by weight, unless otherwise indicated.

Example 1

Control material A—O

4.2 g of phenanthrene quinone, 10.2 g of 2-t-butylanthraquinone, 22.8 g of 1-phenyl-1,2-ethanediol and 9 g of bis(phenacyl) tellurium dichloride were dissolved in 150 g of methylene chloride.

The solution obtained was mixed with 240 g of a 20% solution in methyl ethyl ketone of VINYLITE VAGH (registered trade mark) of Union Carbide and Carbon for a copoly(vinyl chloride/vinyl acetate/vinyl alcohol) (91/3/6)) and 1 ml of 2% of silicone oil in methylene chloride as coating aid.

The resulting coating composition was applied by dip-coating to a polyethylene terephthalate film support at a coverage of 2 g per sq.m of said organo-tellurium compound.

The coating was dried at 40°C with ventilation for 8 h.

The obtained photosensitive recording material A—O was exposed for 10 s through a step wedge with constant 0.3 in the "SPEKTRAPROOF" (registered trade mark) exposure apparatus of Siegfried Theimer GmbH, 6481 Obersatzbach, W. Germany, equipped with a 2000 W lamp emitting with a maximum at about 350 nm.

The exposed material was developed by overall heating for 5 min at 160°C.

Recording material A—1

The preparation of recording material A—1 was the same as described for the control material A—O except that the recording layer was overcoated with a 10% solution in methanol of poly(N-methoxymethylacrylamide) at a dry weight coverage of 4.4 g per sq.m.

Exposure and heating of material A—1 proceeded as described for the control material A—O.

In the accompanying Fig. 1 the curves of density (D) versus photon exposure energy per sq.cm (erg/sq.cm) of the wedge images obtained on the control material A—O (curve A—O) and on the material A—1 (curve A—1) are given.

From these curves is concluded that material A—1 with blocking layer according to the present invention is more than 100 times as sensitive as the control material A—O.

Example 2

Control material B—O

5.4 g of 2-t-butylanthraquinone, 1.4 g of 1-phenyl-1,2-ethane diol, and 1.5 g of bis(phenacyl)-tellurium dichloride were dissolved in 50 ml of methylene chloride.

The obtained solution was mixed with 60 g of a 20% solution of VINYLITE VAGH (registered trade mark) in methyl ethyl ketone and 1 ml of a 2% solution in methylene chloride of silicone oil.

The coating solution was applied by dip-coating to a polyethylene terephthalate support at a coverage of 2.5 g per sq.m of said organo-tellurium compound. Drying proceeded as described for control material A—O of Example 1.

The obtained photosensitive recording material was exposed for 100 s through a stepwedge with constant 0.3 in the already mentioned SPEKTRAPROOF (registered trade mark) apparatus.

The exposed material was developed by overall heating for 5 min at 120°C in the EIKONIX THERMAL PROCESSOR E.D. 199 (EIKONIX is a registered trade mark of EIKONIX Corporation, Burlington, Mass., U.S.A.).

Recording material B—1

The preparation of recording material B—1 was the same as described for material B—O except that a pressure-sensitive adhesive CELLOPHANE (registered trade mark) tape was adhered to the recording layer.

Exposure and heating of material B—1 proceeded as described for the material B—O.

Recording material B—2

The preparation of recording material B—2 was the same as described for material B—0 except that a polyethyleneterephthalate sheet of a thickness of 0.1 mm by means of a drop of silicone oil was adhered to the recording layer.

5 Exposure and heating of material B—2 proceeded as described for the material B—0.

In the accompanying Fig. 2 the curves of density (D) versus photon exposure energy per sq.cm (erg/sq.cm) of the materials B—0, B—1 and B—2 are given.

Example 3

10 *Control material C—0*

5 g of 2-isopropoxy-1,4-naphthoquinone, 17.4 g of 1-phenyl-1,2-ethanediol and 9.42 g of bis(phenacyl)-tellurium dichloride were dissolved in 260 g of tetrahydrofuran.

The obtained solution was mixed with 300 g of a 28% solution of VINYLITE VAGH (registered trade mark) in methyl ethyl ketone and 1 ml of 2% of silicone oil in methylene chloride.

15 The resulting coating composition was applied by dipcoating to a polyethylene terephthalate film support at a coverage of 2.7 g per sq.m of said organo-tellurium compound.

The coating was dried with ventilation at 40°C for 8 h.

The obtained photosensitive recording material was exposed for 10 s through a step wedge with a constant 0.3 in the SPEKTRAPROOF (registered trade mark) exposure apparatus.

20 The exposed material was developed by overall heating at 150°C in a drying stove for 5 min.

Recording material C—1

The preparation of recording material C—1 was the same as described for material C—0 except that the recording layer was overcoated with a solution of 8.5 g of BUTVAR B 76, 1.5 g of CYMEL 300 and 0.05 g of silicone in 100 ml of ethanol. BUTVAR is a registered trade mark of Shawinigan Products Corp., New York, U.S.A. for a polymer of vinyl n-butylal having a molecular weight in the range of 45,000 to 55,000 and a vinyl alcohol unit content of 13%. CYMEL 300 is a trade name of American Cyanamid Company, New York, U.S.A. for hexakis (methoxymethyl)-melamine.

The coating was effected at a coverage of 20 g per sq.m for the vinyl-n-butylal polymer.

30 The exposure proceeded as described for material C—0.

The exposed material C—1 was developed by overall heating at 160°C in a drying stove for 5 min.

In the accompanying Fig. 3 the curves of density (D) versus photon exposure energy per sq.cm (erg/sq.cm) of the materials C—0 and C—1 developed at 160°C are given.

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Claims

1. A photosensitive recording material which contains on a support a recording layer containing in admixture in a binder medium:

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(1) an organo-tellurium compound containing directly linked to a tellurium atom halogen and at least one organic substituent comprising at least one carbonyl group,

(2) a photoreductant,

(3) a hydrogen-donating compound from which hydrogen can be abstracted by the photo-exposed photoreductant,

45 characterized in that one or more blocking layers or a blocking sheet is permanently united with said recording layer, directly or through the intermediary of one or more subbing layers to counteract the penetration of vapour or gas into and the escape of vapour or gas from the recording layer during thermal development after information-wise exposure to ultra-violet and/or visible light of the material, the support and/or the blocking layers or blocking sheet being transparent to said light.

50 2. A material according to claim 1, wherein said blocking layer or sheet is such that when the recording layer of the control material A—0 as defined hereinafter is coated with said layer or sheet the information-wise exposure and thermal development of the coated material yields a tellurium image the maximum optical density of which is at least 0.2 higher than the corresponding maximum optical density of a tellurium image formed under identical exposure and development conditions in an identical material but not coated with said layer or sheet; the preparation and composition of the control material A—0 being as follows:

4.2 g of phenanthrene quinone, 10.2 g of 2-t-butyl-anthraquinone, 22.8 g of 1-phenyl-1,2-ethanediol and 9 g of bis(phenacyl)tellurium dichloride are dissolved in 150 g of methylene chloride; 60 the obtained solution is mixed with 240 g of a 20% solution in methyl ethyl ketone of a copoly(vinyl chloride/vinyl acetate/vinyl alcohol) (90/3/6 by weight) and 1 ml of 2% by weight of silicone oil in methylene chloride as coating aid; the resulting coating composition is dip-coated to a polyethylene terephthalate film support at a coverage of 2 g per sq.m of said organo-tellurium compound and the coating dried at 40°C with ventilation for 8 h, and the information-wise exposure proceeding for 10 s

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through a step wedge with constant 0.3 in an exposure apparatus equipped with a 2000 W lamp emitting with a maximum at about 350 nm.

3. A material according to claim 1 or 2, wherein the blocking layer or sheet is made of a natural or modified natural resin or of a polymeric material prepared by addition polymerization of unsaturated monomers or prepared by polycondensation.

4. A material according to claim 3, wherein the blocking layer or sheet is made of a cellulose ester, of poly(N-methoxy methylacrylamide) or of a polyester.

5. A material according to claim 1 or 2, wherein the blocking layer is made of a cross-linked polymer mass obtained by an acid-catalyzed reaction of a polymer or mixture or polymers containing reactive hydrogen atoms, and an organic compound containing a plurality of etherified N-methylol groups.

6. A material according to claim 1 or 2, wherein the blocking sheet is an adhesive sheet provided with a pressure sensitive adhesive coating applied to the recording material.

7. A material according to any of the claims 1 to 6, wherein the organo-tellurium compound corresponds to the following general formula:



wherein:

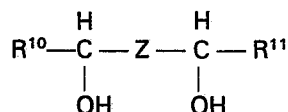
R represents an organic group which by a carbon atom is linked to a tellurium atom and contains at least one carbonyl group,

x is 1, 2 or 3 and

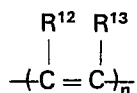
x + y is 4.

8. A material according to any of the preceding claims wherein the photoreductant is an aromatic diketone.

9. A material according to any of the claims 1 to 8, wherein the hydrogen-donating compound corresponds to the following general formula:



wherein each of R^{10} and R^{11} , which may be the same or different, represents hydrogen, a hydrocarbon group, which group may be substituted, or an alkoxy carbonyl group, Z represents a single bond, an ethylene group $-(C \equiv C)-$ or the group



wherein n represents a whole number, and each of R^{12} and R^{13} , which may be the same or different, represents hydrogen, or an alkyl group or together form part of a carbocyclic or heterocyclic ring.

10. A recording process wherein a photosensitive recording material according to any of the claims 1 to 9 is information-wise exposed to ultra-violet and or visible light to which the photoreductant is sensitive, and the exposed material is overall heated to develop a tellurium image in the photo-exposed areas.

Revendications

1. Matériel d'enregistrement photosensible comportant sur un support, une couche d'enregistrement contenant, en mélange dans un milieu liant:

(1) un composé organo-tellurique contenant, en liaison directe avec un atome de tellure, un atome d'halogène et au moins un substituant organique comportant au moins un groupe carbonyle,

(2) un photoréducteur,

(3) un composé donneur d'hydrogène duquel l'hydrogène peut être extrait par le photoréducteur photo-exposé,

caractérisé en ce qu'une ou plusieurs couches d'arrêt ou une feuille d'arrêt est ou sont réunie(s) en permanence avec cette couche d'enregistrement, soit directement, soit par l'intermédiaire d'une ou plusieurs couches adhésives afin de contrecarrer la pénétration et l'échappement d'une vapeur ou d'un gaz respectivement dans et hors de la couche d'enregistrement au cours du développement thermique ayant lieu après avoir exposé l'élément, sous forme d'informations, à la lumière ultraviolette et/ou à la

lumière visible, le support et/ou les couches ou la feuille d'arrêt étant transparents à cette lumière.

2. Matériel suivant la revendication 1, caractérisé en ce que la couche ou la feuille d'arrêt est conçue de telle sorte que, lorsque la couche d'enregistrement du matériel de contrôle A—O défini ci-après est recouvert de cette couche ou de cette feuille, le matériel ainsi revêtu donne après exposition sous forme d'informations et développement thermique, une image de tellure dont la densité optique maximale est supérieure d'au moins 0,2 à la densité optique maximale correspondante d'une image de tellure formée dans des conditions identiques d'exposition et de développement dans un matériel identique, mais non revêtu de cette couche ou de cette feuille, la préparation et la composition du matériel de contrôle A—O étant les suivantes:

10 On dissout 4,2 g de phénanthrène-quinone, 10,2 g de 2-t-butyl-anthraquinone, 22,8 g de l-phényl-1,2-éthane-diol et 9 g de dichlorure de bis(phénacyl)-tellure dans 150 g de chlorure de méthylène; on mélange la solution ainsi obtenue avec 240 g d'une solution d'un copolymère de chlorure de vinyle/acétate de vinyle/alcool vinylique (90/3/6 en poids) à 20% dans de la méthyl-éthyl-cétone et 1 ml d'une huile de silicone à 2% en poids dans du chlorure de méthylène comme adjuvant d'enduction; par immersion, on applique la composition d'enduction ainsi obtenue sur un support pelliculaire de téraphthalate de polyéthylène à raison de 2 g/m² du composé organo-tellurique et l'on sèche la couche ainsi formée à 40°C avec ventilation pendant 8 heures, l'exposition sous forme d'informations ayant lieu pendant 10 s à travers un coin à échelons d'une constante de 0,3 dans un appareil d'exposition "SPECTRAPROOF" (marque commerciale déposée) équipé d'une lampe de 2.000 W émettant avec un maximum se situant à environ 350 nm.

3. Matériel suivant la revendication 1 ou 2, caractérisé en ce que la couche ou la feuille d'arrêt est constituée d'une résine naturelle ou d'une résine naturelle modifiée ou encore d'une matière polymère obtenue moyennant une polymérisation par addition de monomères insaturés ou par polycondensation.

25 4. Matériel suivant la revendication 3, caractérisé en ce que la couche ou la feuille d'arrêt est constituée d'un ester de cellulose, d'un polymère de N-méthoxy-méthylacrylamide ou d'un polyester.

5. Matériel suivant la revendication 1 ou 2, caractérisé en ce que la couche d'arrêt est constituée d'une masse d'un polymère réticulé que l'on obtient en faisant réagir, en présence d'un catalyseur acide, un polymère ou un mélange de polymères contenant des atomes d'hydrogène réactifs et un composé organique contenant plusieurs groupes N-méthylol étherifiés.

30 6. Matériel suivant la revendication 1 ou 2, caractérisé en ce que la feuille d'arrêt est une feuille adhésive dans laquelle un revêtement adhésif sensible à la pression est appliqué au matériel d'enregistrement.

7. Matériel suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que le composé organo-tellurique répond à la formule générale suivante:



dans laquelle:

40 R représente un groupe organique qui est relié à l'atome de tellure par un atome de carbone et qui contient au moins un groupe carbonyle,

x est égal à 1, 2 ou 3, et

x + y est égal à 4.

8. Matériel suivant l'une quelconque des revendications 1 à 7 caractérisé en ce que le photo-réducteur est une dicétone aromatique.

45 9. Matériel suivant l'une quelconque des revendications 1 à 8, caractérisé en ce que le composé donneur d'hydrogène répond à la formule générale suivante:



55 dans laquelle: chacun des radicaux R¹⁰ et R¹¹, qui peuvent être identiques ou différents, représente un atome d'hydrogène, un groupe d'hydrocarbure qui peut être substitué, ou un groupe alcoxycarbonyl, Z représente une liaison simple, un groupe éthylnylène (C = C)_n ou le groupe



où n représente un nombre entier et chacun des radicaux R¹² et R¹³, qui peuvent être identiques ou différents, représente un atome d'hydrogène ou un groupe alkyle ou encore, ensemble, ils font partie d'un noyau carbocyclique ou hétérocyclique.

10. Procédé d'enregistrement, caractérisé en ce qu'un matériel d'enregistrement photosensible suivant l'une quelconque des revendications 1 à 9 est soumis à une exposition, sous forme d'informations, à la lumière ultraviolette et/ou à la lumière visible, lumière à laquelle le photoréducteur est sensible, après quoi, le matériel exposé est chauffé dans son ensemble afin de développer une image de tellure dans les zones photo-exposées.

Patentansprüche

1. Ein photoempfindliches Registriermaterial mit einem Träger und einer Registrierschicht, die vermischt in einem Bindemittel:
 - (1) eine Organotellurverbindung, die, direkt an das Telluratom verbunden, Halogen und mindestens einen organischen Substituenten mit mindestens einer Carbonylgruppe enthält,
 - (2) einen Photoreduktor,
 - (3) eine wasserstoffabgebende Verbindung, der Wasserstoff durch den photobelichteten Photoreduktor entzogen werden kann,
 enthält dadurch gekennzeichnet, dass eine oder mehrere Sperrschichten oder eine Sperrfolie direkt oder durch Vermittlung einer oder mehrerer Haftsichten dauerhaft mit der Registrierschicht verbunden ist, um dem Eindringen und dem Entweichen von Dampf oder Gas in die bzw., aus der Registrierschicht während der Wärmeentwicklung nach der informationsweisen Belichtung des Materials mit UV — und/oder sichtbarem Licht entgegenzuwirken, wobei der Träger und/oder die Sperrschichten bzw. die Sperrfolie dieses Licht durchlassen.
2. Ein Material nach Anspruch 1, dadurch gekennzeichnet, dass die Sperrschicht oder die Sperrfolie deart ist, dass, wenn die Registrierschicht des nachfolgend beschriebenen Kontrollmaterials A—O mit dieser Schicht oder Folie überzogen ist, die informationsweise Belichtung und die Wärmeentwicklung des beschichteten Materials ein Tellurbild ergeben, dessen optische Densität um mindestens 0,2 höher ist als die übereinstimmende optische Densität eines unter identischen Belichtungs — und Entwicklungsbedingungen erzeugten Tellurbildes in einem identischen Material, das jedoch nicht mit dieser Schicht oder Folie überzogen wurde, wobei die Herstellung und die Zusammensetzung des Kontrollmaterials A—O wie folgt sind:

4,2 g Phenanthrenchinon, 10,2 g 2-t-Butylanthrachinon, 22,8 g 1-Phenyl-1,2-äthandiol und 9 g Bis(phenacyl)-tellurdichlorid werden in 150 g Methylenchlorid gelöst; die erhaltene Lösung wird mit 240 g einer 20%igen Lösung eines Mischpolymeren aus Vinylchlorid, Vinylacetat und Vinylalkohol (90/3/6 gew.%) in Methyläthylketon und 1 ml einer 2 gew.-%igen Silikonöllösung in Methylenchlorid als Giesszusatz gemischt; die erhaltene Giesszusammensetzung wird nach dem Tauchverfahren in einem Verhältnis von 2 g der Organotellurverbindung auf einen Polyäthylenterephthalatfilmträger aufgetragen und die Schicht unter Ventilation 8 h bei 40°C getrocknet, wobei die informationsweise Belichtung 10 s durch einen Stufenkeil der Konstante 0,3 in einem "SPEKTRAPROOF" (eingetragenes Warenzeichen)-Belichtungsapparat, der mit einer 2000-W-Lampe ausgerüstet ist, die mit einem Maximum bei etwa 350 nm emittiert, stattfindet.
3. Ein Material nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, dass die Sperrschicht oder Sperrfolie aus einem natürlichen oder einem natürlichen, modifizierten Harz, oder aus einer Polymermaterial besteht das durch Additionspolymerisation ungesättigter Monomere oder durch Polykondensation hergestellt wurde.
4. Ein Material nach Anspruch 3, dadurch gekennzeichnet, dass die Sperrschicht oder Sperrfolie aus einem Celluloseester, Poly(N-methoxymethylacrylamid) oder einem Polyester besteht.
5. Ein Material nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, dass die Sperrschicht aus einer verknüpften Polymermasse besteht, die durch eine säurekatalysierte Reaktion eines reaktionsfähigen Wasserstoffatoms enthaltenden Polymeren oder einer Mischung solcher Polymeren und einer organischen, mehrere verätherte N-Methylolgruppen enthaltenden Verbindung erhalten wird.
6. Ein Material nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, dass die Sperrfolie eine Klebfolie ist, die mit einer druckempfindlichen, auf das Registriermaterial aufgetragenen Klebeschicht versehen ist.
7. Ein Material nach irgendeinem der Ansprüche 1—6 dadurch gekennzeichnet, dass die Organotellurverbindung der allgemeinen Formel



entspricht, in der bedeuten:

- R eine organische Gruppe, die über ein Kohlenstoffatom mit dem Telluratom verbunden ist und mindestens eine Carbonylgruppe enthält,
 x 1, 2 oder 3, und
 x + y 4.

8. Ein Material nach irgendeinem der vorangehenden Ansprüche dadurch gekennzeichnet, dass der Photoreduktor ein aromatisches Diketon ist.

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9. Ein Material nach irgendeinem der Ansprüche 1—8 dadurch gekennzeichnet, dass die wasserstoffabgebende Verbindung der allgemeinen Formel



10 entspricht in der bedeuten: R¹⁰ und R¹¹ (gleich oder verschieden) je Wasserstoff, eine gegebenenfalls substituierte Kohlenwasserstoffgruppe oder eine Alkoxy-carbonylgruppe, Z eine Einfachbindung, eine Äthylengruppe —(C = C)_n oder die Gruppe



20 in der n eine ganze Zahl ist, und R¹² und R¹³ (gleich oder verschieden) je Wasserstoff oder eine Alkylgruppe bedeuten, oder zusammen ein Teil eines Kohlenstoff — oder eines Heteroringes sind.

10. Ein Registrierverfahren, dadurch gekennzeichnet, dass ein photoempfindliches Registriermaterial nach irgendeinem der Ansprüche 1—9 informationsweise mit UV — oder sichtbarem Licht belichtet wird, für das der Photoreduktor empfindlich ist, und das belichtete Material zur Entwicklung eines Tellurbildes an den photobelichteten Stellen gleichmässig erhitzt wird.

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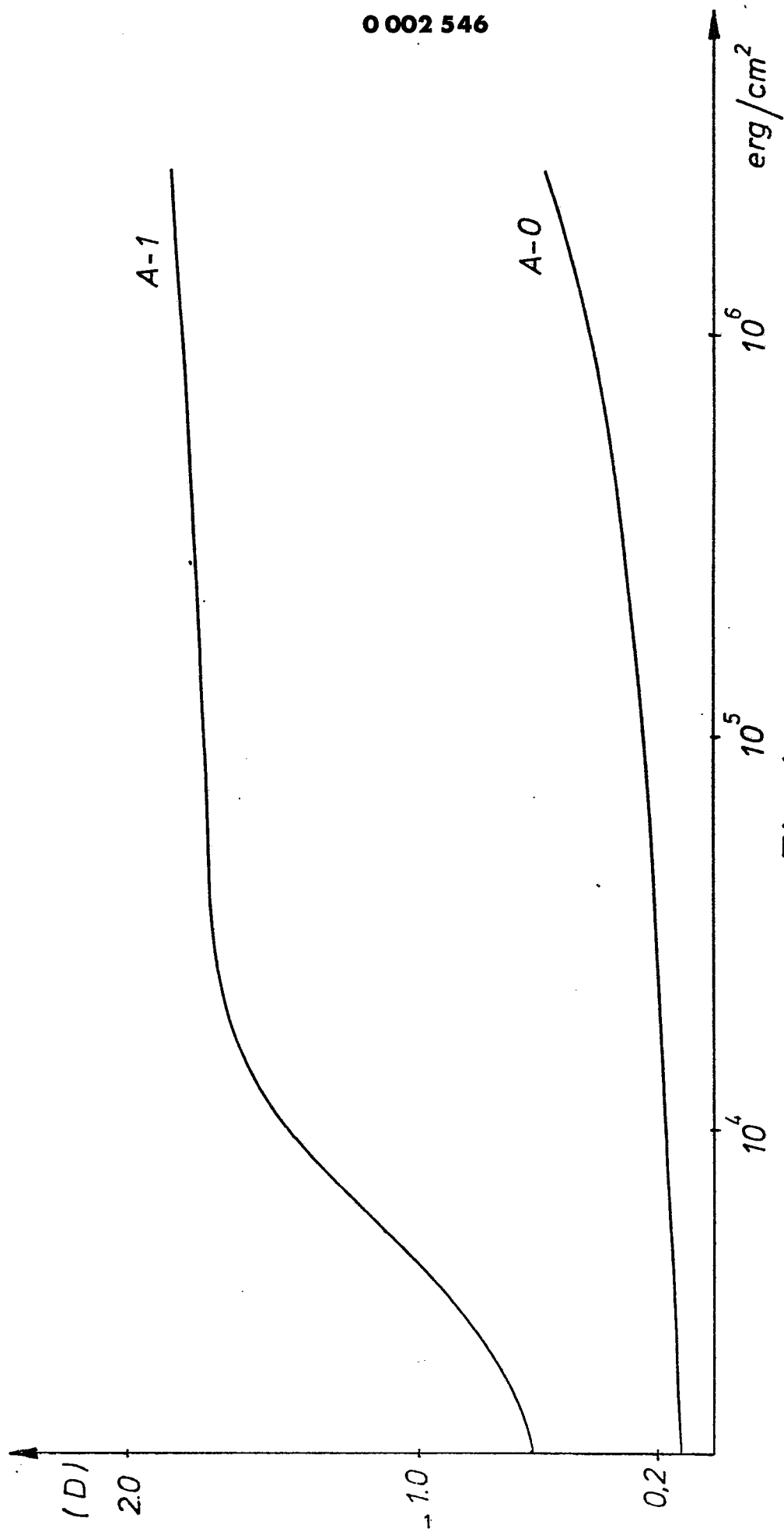


Fig. 1

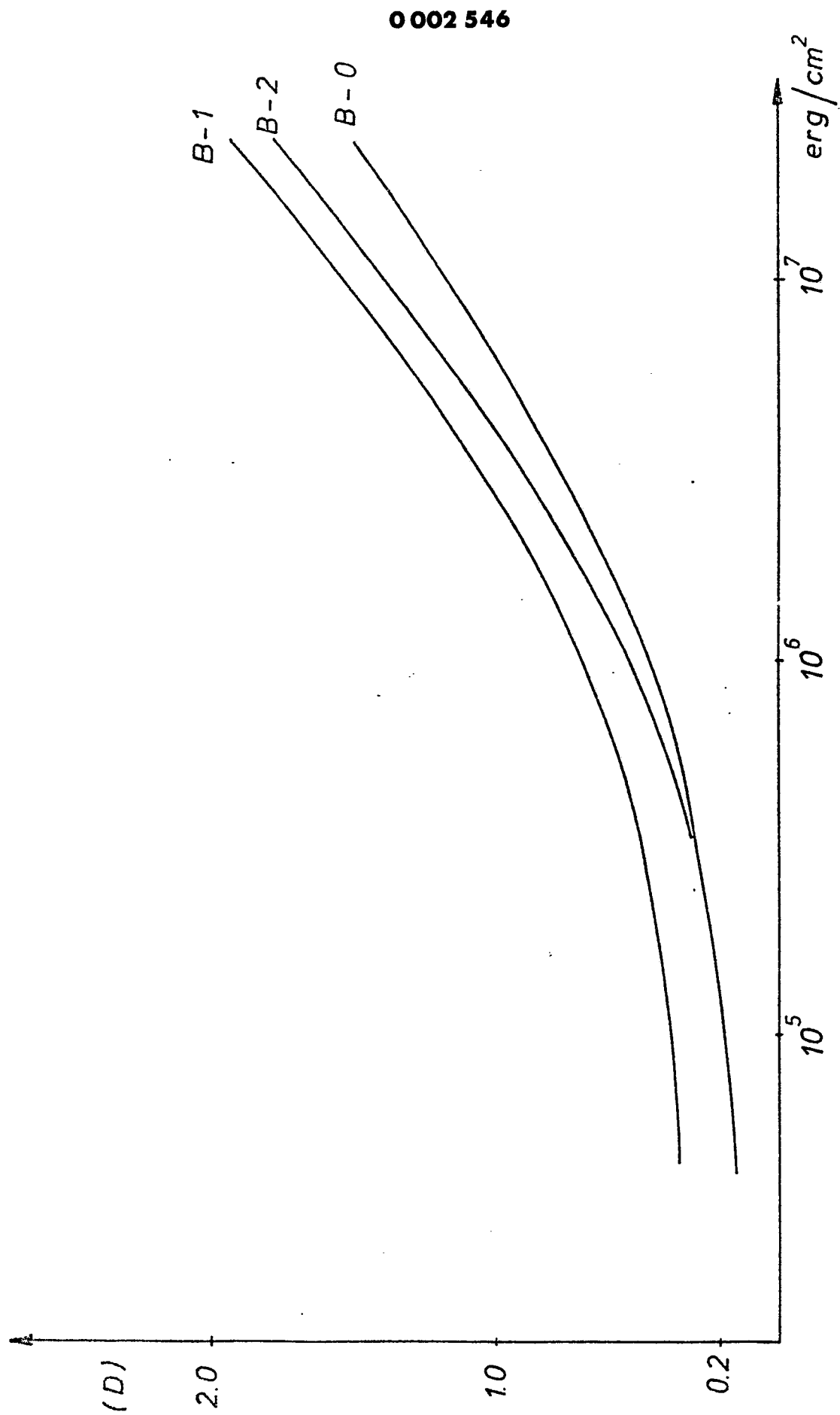


Fig. 2

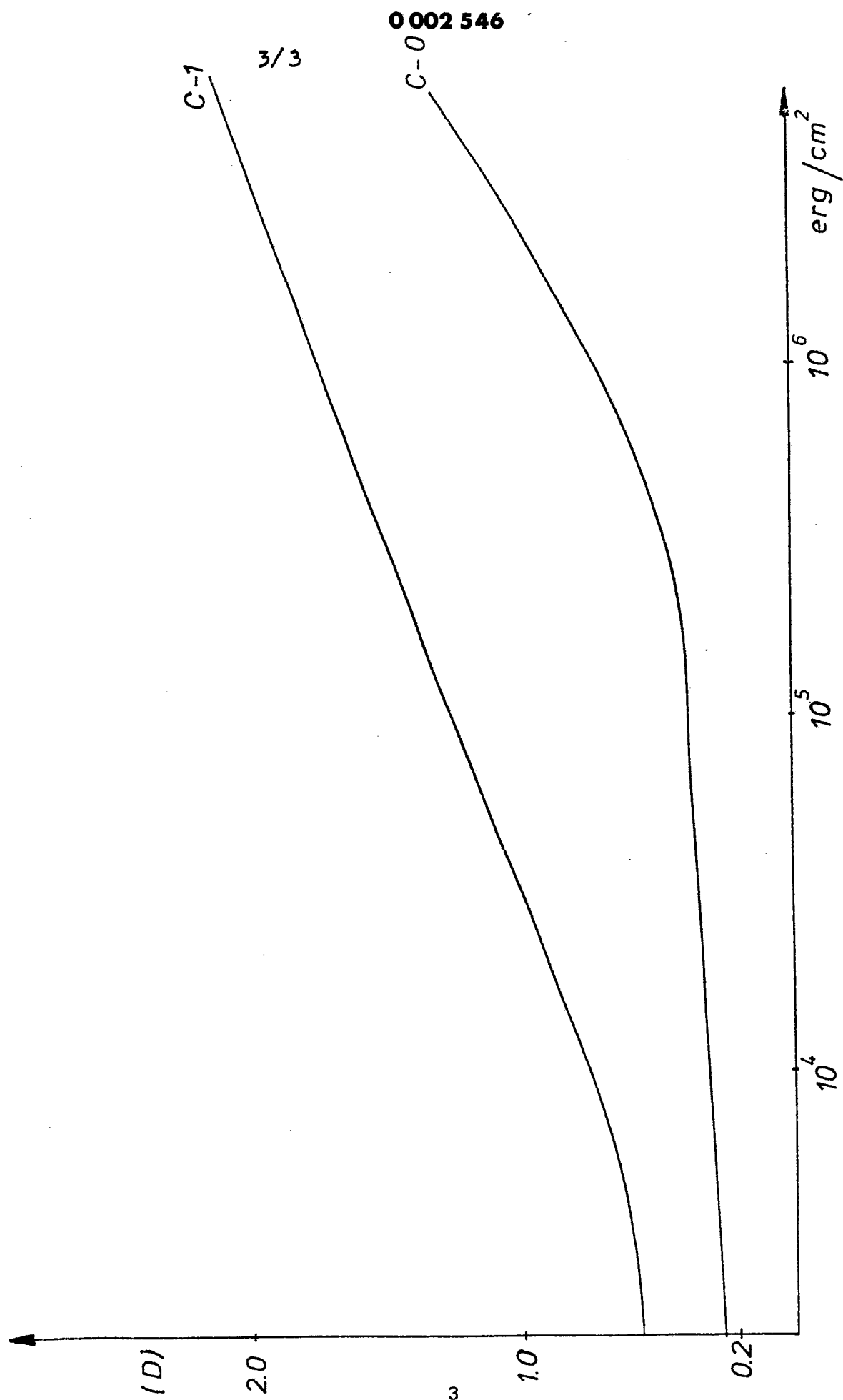


Fig. 3