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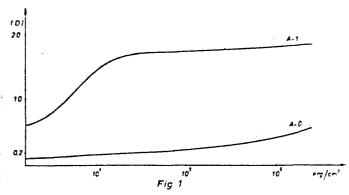
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- (Si) Improved photosensitive recording material and a method of recording information by exposure of said material to information-wise modulated activating electro-magnetic radiation.
- (57) A photosensitive recording material is described which upon information-wise exposure and heat-development forms a tellurium image. The material contains on a support a recording layer containing in admixture in a binder medium:
- (1) as imaging substance an organo-tellurium compound 20 containing directly linked to a tellurium atom halogen and at least one organic substituent comprising at least one carbonyl group,
- (2) a photoreducant, and

(3) a hydrogen-donating compound from which hydrogen can be abstracted by the photo-exposed photoreductant. The said material needs less exposure energy by having united with said recording layer directly or through the intermediary of one or more subbing layers, a blocking layer or sheet that counteracts the penetration of vapour or gas into and the escape of vapour or gas from the recording layer N during thermal treatment after photo-exposure of the material, the support and/or the blocking layer or sheet being transparent for actinic radiation.



Improved photosensitive recording material and a method of recording information by exposure of said material to information-wise modulated activating electro-magnetic radiation.

The present invention relates to improved photosensitive recording material and a method of recording information by exposure of said material to informationwise modulated activating electro-magnetic radiation.

In the published German Patent Application (Dt-OS)
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,
15 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
20 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:

PQ exposure 
$$^{1}PQ \longrightarrow ^{3}PQ$$
  
25  $^{3}PQ + 2 RH \longrightarrow PQ.H_{2} + R-R$ 

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 $(R^{1})_{2}$ .Te.Cl<sub>2</sub> + 2 PQ.H<sub>2</sub>  $\rightarrow$  2 PQ + 2  $R^{1}$ H + Te + 2 HCl wherein :

PQ is a photoreductant e.g. phenanthrenequinone,

1PQ is the first excited singlet of said quinone,

3PQ is the triplet state of said quinone,

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

PQ.H<sub>2</sub> is the photoreductant in reduced state, and

(R<sup>1</sup>)<sub>2</sub>·Te.Cl<sub>2</sub> is a reducible organo-tellurium compound

wherein R<sup>1</sup> is e.g. (C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>).

A disadvantage associated with recording materials containing these compounds is their rather low photosensitivity.

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) as imaging substance 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 that a blocking layer or 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

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layer during thermal treatment after photoexposure of the material, the support and/or said blocking layer or sheet in order to allow the exposure with actinic radiation of the recording layer being transparent for said radiation.

By "actinic radiation" is understood here electromagnetic radiation e.g. ultraviolet radiation and/or visible light to which the recording layer is sensitive for the image formation. The wording "blocking layer" includes here a single layer as well as a plurality of said layers.

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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

15 Example 1 is coated with said layer or sheet the described image-wise exposure and thermal processing 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

20 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: pol(isobutyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), copolymers of GV.1005

vinyl-n-butyral, a copoly(vinyl acetate/vinyl chloride), a copoly(acrylonitrile/butadiene/styrene), a copoly(vinyl acetate/vinyl acetate/vinyl acetate/vinyl alcohol) and poly(N-methoxy-methyl acrylamide).

Apart from the polymers produced by addition polymerization of unsaturated monomers, likewise polymers
prepared by polyaddition, e.g. polyurethanes or polycondensation, e.g. 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

15 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 -N-CH<sub>2</sub>OCH<sub>2</sub> groups as cross-linking agent.

A polymer containing reactive hydrogen atomsforming part of free hydroxyl groups and appropriate for acid-catalyzed cross-linking with compounds containing
25 etherified N-methylol groups is, e.g., a polyester comprising free hydroxyl groups, a polyvinyl acetal in which part of the hydroxyl groups of the polyvinyl alcohol starting product has 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.
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vinyl acetate units. The molecular weight of the polyvinyl butyral may be within a troad range but is preferably between 40,000 and 55,000. Polyvinyl butyrals characterized by an intrinsic viscosity of 0.75 to 1.25 dl.g<sup>-1</sup> 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:

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N-CH<sub>2</sub>OCH<sub>3</sub> + H-R H+ R-CH<sub>2</sub>R + CH<sub>3</sub>OH wherein R represents the organic group of the polymer involved.

The reaction proceeds preferably at elevated tem-5 perature. 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 means in the form of a coating on the recording layer is preferably at least 5  $\mu m$  e.g. in the range of 5 to 200  $\mu m$ .

The blocking coating 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 GV.1005

medium that does not disculve or does not give rise to swelling of the hinder of the recording layer. A suitable blocking coating 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 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.

20 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:

$$R_x$$
TeCl $_y$ 

25 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

 $30 \quad x + y = 4.$ 

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

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A preferred class of insging agents are organdtellurium compounds corresponding to the following creeral formula:

$$(\text{Ar} - \text{CO} - \text{CH}_2)_2 \text{TeOl}_2$$

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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 carbocydic aromatic ring.

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

# Table 1

30	Photoreductant	Spectral sensitivity range (nm)		
	9,10-phenanthrenequinone	200 - 400 - 500		
		U.V. visible		
	1,1'-dibenzoylferrocene	400 - 600		
	1-phenyl-1,2-propanedions	400 - 500		

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	2-hydroxy-1,4-naphthoguinone	400 <b>- 5</b> 00 400 <b>-</b> 450
5	furil	400 - 480
	diacetylferrocene acetylferrocene	400 - 450 400 - 450
	1,4-bis(phenyl glyoxal)-benzene c-naphthoquinone	400 - 500 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; acetorhenone; 1,5-diphenyl-1,3,5-pentanetrione; ninhydrin: 4,4'-dibromobenzophenone; 2-t-butylanthraouinone and 1,8-dichloroanthraguinone. 15

In the reduction of said organo-tellurium compounds 9,10-phenanthrenequinone and 2-t-butylanthraquinone 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 photoreductant correspond to the following general formula :

$$R^{10} - C - Z - C - R^{11}$$

wherein :

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each of R<sup>10</sup> and R<sup>11</sup>, 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, GV.1005

a hydroxyalkyl group, a cycloalkyl group or an aryl group, or an alkoxycarbonyl group e.g. a  $\rm C_2H_5-0-CO-group$  .

Z represents a single bond, an ethynylene group

5 
$$\frac{\left[-\left(C\equiv C\right)\right]_{n}}{n}$$
 or the group

$$\frac{R^{12} R^{13}}{C} = C \frac{1}{n}$$

wherein n represents a whole number e.g. 1 and 2, and each of R<sup>12</sup> and R<sup>13</sup>, 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

5 are listed in the following table 2 and can be found in
the German Patent Application P 2719023.

Table 2

30

20	No. of the compound	R <sup>10</sup>	Z	<sub>R</sub> 11	(BP)	ing point °C or mel- point (MP)°C
25	1	H		H	BP	198
	2	<⇒-	-	H	MP	67
	3	H <sub>3</sub> C- H <sub>3</sub> C- H	_	H	BP	189
	4	H <sub>3</sub> C-	-	-CH <sub>3</sub>	BP	183
	.5	н	-C≡C-	H	MP	52-54
	6	H	-<>>-	H	MP	112
	7	HO(CH <sub>2</sub> ) <sub>4</sub> -	-	H	BP 1'	78/5 mm Hg
	8	HO(CH <sub>2</sub> ) <sub>4</sub> - C <sub>2</sub> H <sub>5</sub> OCO-	-	С <sub>2</sub> H <sub>5</sub> 0-СО-	BP	280

The preparation of these compounds is known to those skilled in the art. A particularly suitable hydrogendonating 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 GV.1005

according to the German Patent Application No.P 2802666
increases the photographic screen of the record—
ing material. From said organic reducing agent precursor
by the action of an acid, e.g. HCl formed in the imaging

5 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—

10 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
25 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 30 precursors are listed in the following table 3.

# Table 3

	T		
5	Compound no.	Chemical structure	Melting scint (MP) or boil- ing point (BP) °C
	1	OCOCH <sub>3</sub>	BP 140-144 (0,05 mm Hg)
10		och <sub>3</sub>	
	2	OCOCH <sub>2</sub> -N	MP about 200
15		OCH <sub>3</sub>	
	3		MP about 200
20		OCOCH <sub>3</sub>	
25	4		MP 132
<i>د</i> ح		H <sub>2</sub> C N-CONH-	
30	. 5		MP 181
		H <sub>2</sub> C — C=0	

	6		MP 135
5		H <sub>2</sub> C N-CONHC <sub>2</sub> H <sub>5</sub> H <sub>2</sub> C - C=0	
10	7		MP 182
		H <sub>2</sub> C N-CONHCO-	
15	8		MP 164
		H <sub>2</sub> C N-CONHCO- H <sub>3</sub> C-C C=O	
20	9		MP 97
25	Andrews and the state of the st	H <sub>2</sub> C N-COCH <sub>2</sub> Cl H <sub>2</sub> C - C=O	

The preparation of these compounds is described in said German Patent Application P 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 socalled 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 15 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 abovementioned 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
25 the coating composition by evaporation so that a solid
photographic recording layer on a properly chosen support
is left. The supports may be of any 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-GV.1005

donating compound in the Ferably 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.

10 said material to activating electromagnet's radiation to which the photo-reductant is sensitive and overall heading to develop a tellurium image in the recording material.

An information-wise ultraviolet exposure is normally used in combination with an aromatic diketone as photo15 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.

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

#### Example 1

#### 30 Control material A-O

4.2 g of phenanthrene quinche, 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 450 g of methylene chloride.

The solution obtained was mixed with 240 g cf a 20 % solution in methyl ethyl ketone of VINYLITE VAGH (trade name 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 10 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 15 0.3 in the "SPEKTRAPROOF" (trade name) 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 20 heating for 5 min at  $160^{\circ}\text{C}$ 

### Recording material A-1

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The preparation of recording material A-1 was the same as described for the control material A-0 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 30 (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 GV.1005

with blocking layer according to the present invention is more than 400 times as sensitive as the control material A-O.

#### Example 2

#### 5 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 % 10 solution of VINYLITE VAGH (trade name) in methyl ethyl ketone and 1 ml of a 2 % solution in methylene chloride of silicone cil.

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 (trade name) 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 trade name of EIKONIX Corporation,

25 Burlington, Mass., U.S.A.).

## Recording material B-1

The preparation of recording material B-1 was the same as described for material B-0 except that a pressure-sensitive adhesive cellophane (trade name) tape 30 was adhered to the recording layer.

Exposure and heating of material B-1 proceeded as described for the material B-0.

## Recording material B-2

The preparation of recording material B-2 was the GV.1005

same as described for material B-O 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-O, B-1 and B-2 are given.

## 10 Example 3

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#### Control material C-O

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 (trade name) in methyl ethyl ketone and 1 ml of 2 % of silicone oil in methylene chloride.

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

The coating was dried with ventilation at 40°C for 25 8 h.

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

The exposed material was developed by overall heating 30 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 GV.1005

of BUTVAR B 76, 1.5 g of MEL 300 and 0.05 g of silicone in 100 ml of commun. BUTVAR is a tradename of Shawinigan Products Commun, New York, U.S.A. for a polymer of vinyl n-butyral 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 10 sq.m for the vinyl-n-butyral polymer.

The exposure proceeded as described for material C-C. 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-O and C-1 developed at 160°C are given.

#### WHAT WE CLAIM IS :

- 1. A photosensitive recording material which contains on a support a recording layer containing in admixture in a binder medium:
- 5 (1) as imaging substance 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,
- 10 (3) a hydrogen-donating compound from which hydrogen can be abstracted by the photo-exposed photoreductant, characterized in that a blocking layer or sheet is permanently united with said recording layer, directly or through the intermediary of one or more subbing layers

  15 to counteract the penetration of vapour or gas into and the escape of vapour or gas from the recording layer during thermal treatment after photo-exposure of the material, the support and/or the blocking layer or sheet being transparent for actinic radiation.
- 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-O as defined hereinbefore is coated with said layer or sheet the described image-wise exposure and thermal processing of the coated material
- 25 yields a tellurium image the maximum optical density of which is at least 0.2 higher than the corresponding maximum

optical density of a religious image formed under identical exposure and order tiles conditions in an identical material but not obsted with said layer or sheet.

- 3. A material according to claims 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 polyaddition or polycondensation.
- 4. A material according to claim 3, wherein the blocking 10 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 of 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 20 pressure sensitive adhesive coating.
  - 7. A material according to any of the claims 1 to 6, wherein the organo-tellurium compound corresponds to the following general formula:

# $R_x$ TeCl<sub>y</sub>

25 wherein:

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

x is 1, 2 or 3 and

- $x_{\pm y}$  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, GV.1005 GB

wherein the hydrogen-dresting compound corresponds to the following general fermula :

$$R^{10} - \begin{array}{c} H \\ - 0 \\ 0 \\ 0 \\ H \end{array} - \begin{array}{c} H \\ - 0 \\ 0 \\ 0 \\ 0 \\ H \end{array}$$

wherein:

5

10

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each of R<sup>10</sup> and R<sup>11</sup>, 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, or an alkoxycarbonyl group,

Z represents a single bond, an ethynylene group  $\frac{1}{2}$  (CEO- $\frac{1}{2}$ n or the group  $\frac{R^{12}}{C} = \frac{R^{13}}{n}$  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 20 information-wise exposed to electromagnetic radiation to which the photo-reductant is sensitive, and the exposed material is overall heated to develop a tellurium image in the photo-exposed areas.

