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(54) Thermosensitive recording material

Wärmeempfindliches Aufzeichnungsmaterial

Matériau d'enregistrement thermosensible

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FR-A- 2 225 771 **US-A- 3 031 329**

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Description

1. Field of the Invention

The present invention relates to a recording material suited for use in direct thermal imaging.

2. Background of the Invention

Thermal imaging or thermography is a recording process wherein images are generated by the use of imagewise modulated thermal energy.

In thermography two approaches are known :

1. Direct thermal formation of a visible image pattern by imagewise heating of a recording material containing matter that by chemical or physical process changes colour or optical density.
2. Thermal dye transfer printing wherein a visible image pattern is formed by transfer of a coloured species from an imagewise heated donor element onto a receptor element.

Thermal dye transfer printing is a recording method wherein a dye-donor element is used that is provided with a dye layer wherefrom dyed portions or incorporated dye is transferred onto a contacting receiver element by the application of heat in a pattern normally controlled by electronic information signals.

The optical density of transparencies produced by the thermal transfer procedure is rather low and in most of the commercial systems - in spite of the use of donor elements specially designed for printing transparencies - only reaches 1 to 1.2 (as measured by a Macbeth Quantalog Densitometer Type TD 102). However, for many application fields a considerably higher transmission density is asked for. For instance in the medical diagnostical field a maximal transmission density of at least 2.5 is desired.

A survey of "direct thermal" imaging methods is given in the book "Imaging Systems" by Kurt I. Jacobson-Ralph E. Jacobson, The Focal Press - London and New York (1976), Chapter VII under the heading "7.1 Thermography". Thermography is concerned with materials which are not photosensitive, but are sensitive to heat or thermosensitive. Imagewise applied heat is sufficient to bring about a visible change in a thermosensitive imaging material.

Most of the "direct" thermographic recording materials are of the chemical type. On heating to a certain conversion temperature, an irreversible chemical reaction takes place and a coloured image is produced.

A wide variety of chemical systems has been suggested some examples of which have been given on page 138 of the above mentioned book of Kurt I. Jacobson et al., describing the production of a silver metal image by means of a thermally induced oxidation-reduction reaction of a silver soap with a reducing agent.

According to US-P 3,080,254 a typical heat-sensitive copy paper includes in the heat-sensitive layer a water-insoluble silver salt, e.g. silver stearate and an appropriate organic reducing agent, of which 4-methoxy-1-hydroxy-dihydronaphthalene is a representative. Localized heating of the sheet in the thermographic reproduction process, or for test purposes, by momentary contact with a metal test bar heated to a suitable conversion temperature in the range of about 90-150 °C, causes a visible change to occur in the heat-sensitive layer. The initially white or lightly coloured layer is darkened to a brownish appearance at the heated area. In order to obtain a more neutral colour tone a heterocyclic organic toning agent such as phthalazinone is added to the composition of the heat-sensitive layer. The heat-sensitive copying paper is used in "front-printing" or "back-printing" as illustrated in Figures 1 and 2 of US-P 3,074,809.

As described in Handbook of Imaging Materials, edited by Arthur S. Diamond - Diamond Research Corporation - Ventura, California, printed by Marcel Dekker, Inc. 270 Madison Avenue, New York, New York 10016 (1991), p. 498-499 in direct thermal printing signals are converted to electric pulses and then through a driver circuit selectively transferred to a thermal printhead. The thermal printhead consists of microscopic heat resistor elements, which convert the electrical energy into heat via the Joule effect. The electric pulses thus converted into thermal signals manifest themselves as heat transferred to the surface of the thermal paper wherein the chemical reaction resulting in colour development takes place.

According to the lastmentioned book (ref. p. 499-551) in the past several systems were developed for direct thermal imaging of which the leuco dye system has found commercial use. Optical density obtained with embodiments of said system is usually not higher than 2 and requires mixtures of leuco dye compounds to produce neutral black.

Heat-sensitive copying materials including a redox-system of light-insensitive organic silver salt and organic reducing agent in the presence of a toning agent may well provide relatively high maximal optical densities but suffer normally from a too high minimal optical density and rather poor stability under conditions of moderate heating (about 50 °C) and relative humidity in the range of 30 to 70 %.

On the one hand the organic reductor should not react prematurely with the organic silver salt under moderate heating conditions but on the other hand it should be an effective reductor at temperatures provided in direct thermal

imaging e.g. by thermal printheads. As described in the above mentioned book "Handbook of Imaging Materials", p. 502 in printheads for direct thermal imaging the surface temperature may reach 300-400 °C while the copying paper contacts the printheads at pressures of 200-500 g/cm² to ensure sufficient heat transfer.

From US-A- 3,031,329 spiroindane is known to be an organic reductor for thermosensitive organic silver salts.
From FR-A- 2,225,771 hydroxyindane is known for the same purpose.

3. Objects and Summary of the Invention

It is an object of the present invention to provide a recording material suited for use in direct thermal imaging which material contains in a recording layer a binder and a substantially light-insensitive organic silver salt in thermal working relationship, e.g. admixture, with an organic reducing agent by means of which silver images having a maximal density above 3 can be obtained without substantial density increase at temperatures up to 50 °C providing thereby satisfactory storage stability of the non-imaged recording material, and showing practically no decrease in imaging capability after a conditioning treatment at 57 °C and relative humidity of 34 %.

It is a further object of the present invention to provide a recording process which comprises exposing to a heat pattern a recording material having the above enumerated properties.

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

A recording material suited for use in direct thermal imaging is provided, wherein said recording material comprises : (i) a support and (ii) at least one imaging layer containing uniformly distributed in a polymeric binder (1) a substantially light-insensitive organic silver salt in thermal working relationship with (2) at least one organic reducing agent, characterized in that said organic reducing agent is a polyhydroxy spiro-bis-indane.

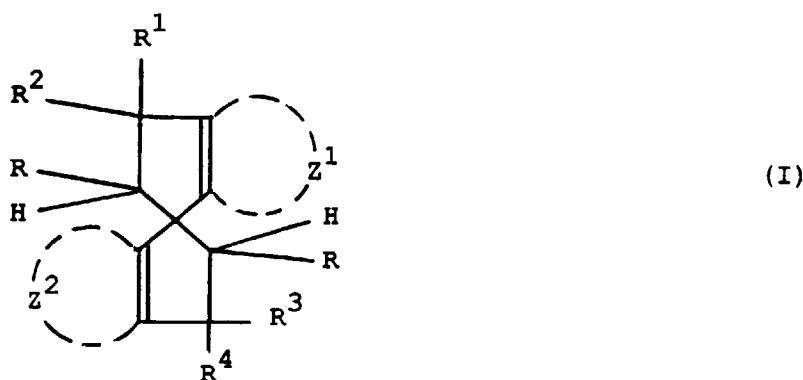
By "thermal working relationship" is meant here that said substantially light-insensitive organic silver salt and said reducing agent by means of heat can react to form metallic silver. For that purpose said ingredients (1) and (2) may be present in a same layer or different layers wherefrom by heat they can come into reactive contact with each other, e.g. by diffusion or mixing in the melt. A heat-sensitive recording material containing silver behenate and 4-methoxy-1-naphthol as reducing agent in adjacent binder layers is described in Example 1 of US-P 3,094,417.

The present invention includes likewise the use of said recording material in direct thermal imaging.

In the thermographic process according to the present invention the application of the heat pattern proceeds in direct thermal imaging mode, whereby is meant that during the application of said heat pattern a visible image is formed in said recording material without the aid of substances that are thermally pattern-wise transferred thereon and/or therein.

4. Detailed Description of the Invention

Polyhydroxy spiro-bis-indane compounds suited for use according to the present invention are within the scope of following general formula (I):



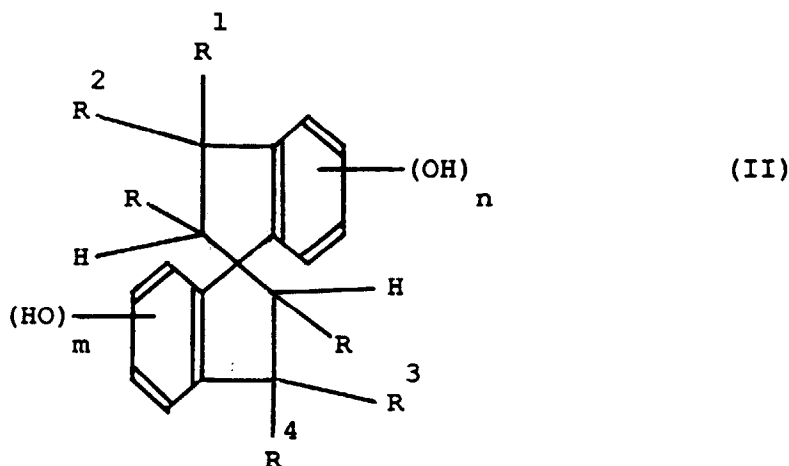
wherein :

R represents hydrogen or alkyl, e.g. methyl or ethyl, each of R¹ and R² (same or different) represents H, an alkyl group, e.g. methyl, ethyl or propyl, an alkenyl group or a cycloalkyl group, e.g. cyclohexyl group, or R¹ and R² together represent the atoms necessary to close a homocyclic non-aromatic ring, e.g. a cyclohexyl ring, each of R³ and R⁴ (same or different) represents H, an alkyl group, e.g. methyl, ethyl or propyl, an alkenyl group

or a cycloalkyl group, e.g. cyclohexyl group, or R³ and R⁴ together represent the atoms necessary to close a homocyclic non-aromatic ring, e.g. cyclohexyl,
 each of Z¹ and Z² (same or different) represents the atoms necessary to close an aromatic ring or ring system, e.
 g. benzene ring, substituted with at least two hydroxyl groups in ortho- or para-position and optionally further
 substituted with at least one hydrocarbon group, e.g. an alkyl or aryl group.

A preferred recording material according to the present invention contains a polyhydroxy spiro-bis-indane that is di-alkyl substituted in both of its indane rings, more particularly in the 3-and 3'-position of the spiro-bis-indane.

A particularly preferred recording material according to the present invention contains a polyhydroxy spiro-bis-indane compound corresponding to the following general formula (II) :



wherein :

R represents hydrogen or alkyl, e.g. methyl or ethyl,
 each of R¹ and R² (same or different) represents, an alkyl group, preferably methyl group or a cycloalkyl group, e.g. cyclohexyl group,
 each of R³ and R⁴ (same or different) represents, an alkyl group, preferably methyl group or a cycloalkyl group, e.g. cyclohexyl group, and
 n is a positive integer 2 or 3,
 m represents zero or is a positive integer 1, 2 or 3, and at least two of the hydroxyl groups of said formula are in ortho- or para-position.

Particularly useful in the process of the present invention are the polyhydroxy-spiro-bis-indane compounds described in US-P 3,440,049 as photographic tanning agent, more especially 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-1,1'-spiro-bis-indane (called indane I) and 3,3,3',3'-tetramethyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indane (called indane II). Indane is also known under the name hydrindene.

The preparation of indane (I) can proceed by condensation of catechol with acetone such as disclosed by Baker, J. Chem. Soc., 1943, pp. 1678-81.

The preparation of indane (II) can proceed by the condensation of polyhydric phenols with acetone as disclosed by Fischer, Furling and Grant, J. Am. Chem. Soc., 58, pp. 820-22 (1936). Alkyl and hydroxy substituted spiro-bis-indanes where the hydroxyls are in ortho- or para-position of the aromatic rings can also be prepared as described in German patent 1,092,648. Other preparation methods are described in German patent 1,084,260, JP 03148232 A2, JP 02286642 A2, JP 02286641 A2, and Tetrahedron Lett., (34), 3707-10 in the article titled : "New Spirobiindanetetrols from 3-tert.-Alkylpyrocatechols". Polyhydroxy spiro-bis-indane compounds within the scope of the above general formulae (I) or (II) such as 1,1'-spirobi[1H-indene]-4,5,5',6,6',7'-hexol, 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl; 1,1'-spirobi[indan]-5,5',6,6'-tetrol, 3-methyl-3-ethyl, 3'-methyl, 3'-ethyl; 1,1'-spirobi[indan]-5,5',6,6'-tetrol, 2-ethyl-3,3-dimethyl-3,3'-dipropyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 3,3'-diethyl-2,2',3,3'-tetrahydro-2,3,3'-trimethyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 2,2'-diethyl-2,2',3,3'-tetrahydro-3,3,3',3'-tetrapropyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 3,3'-diethyl-2,2',3,3'-tetrahydro-2,2',3,3'-tetramethyl; 1,1'-spirobi[1H-indene]-4,4',5,5',6,6'-hexol, 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 3,3'-diethyl-2,2',3,3'-tetrahydro-3,3'-dimethyl; 1,1'-spirobi[1H-in-

dene]-5,5',6,6',7,7'-hexol, 2,2',3,3'-tetrahydro-3,3,3',3'-teramethyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 2,2',3,3'-tetrahydro-3,3,3',3',7,7'-hexamethyl; and 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol, 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl are further described in the documents referred to in the following Chemical Abstracts items mentioned under their CAS registry number (RN) 122465-37-6, 121734-42-7, 109733-95-1, 90146-64-8, 73944-85-1, 73944-84-0, 65192-09-8, 55468-60-5, 32737-33-0, and 32737-32-9.

The polyhydroxy spiro-bis-indane reducing agents according to the above general formulae (I) or (II) may be used in a thermographic recording material according to the present invention in combination with other reducing agents, e.g. sterically hindered phenols operating as auxiliary reducing agents that on heating become reactive partners in the reduction of a non-light-sensitive silver salt such as silver behenate, or are used in combination with bisphenols as described in US-P 3,547,648.

A survey of conventional organic reducing agents containing active hydrogen attached through O, N or C, for example with o-alkyl- or cycloalkyl-substituted phenols, aminophenols, methoxynaphthol derivatives, bis- β -naphthols, hydroxycoumaranes and hydroxychromanes, is given in GB-P 1,439,478. Other optionally used reducing agents in conjunction with said polyhydroxy spiro-bis-indanes to give increased image density are the metal ion image amplifier materials such as stannous stearate described in US-P 3,460,946 and 3,547,648.

In a first embodiment of the method according to the present invention the pattern-wise or image-wise heating of the recording material proceeds by Joule effect heating in that selectively energized electrical resistors of a thermal head array are used in contact or close proximity with said recording layer.

In a special embodiment of image-wise electrically heating the recording element, an electrically resistive ribbon is used consisting e.g. of a multilayered structure of a carbon-loaded polycarbonate coated with a thin aluminium film (ref. Progress in Basic Principles of Imaging Systems - Proceedings of the International Congress of Photographic Science Köln (Cologne), 1986 ed. by Friedrich Granzer and Erik Moisar - Friedr. Vieweg & Sohn - Braunschweig/Wiesbaden, Figure 6. p. 622). Current is injected into the resistive ribbon by electrically addressing a print head electrode contacting the carbon-loaded substrate, thus resulting in highly localized heating of the ribbon beneath the energized electrode. In the present embodiment the aluminium film makes direct contact with the heat-sensitive recording layer or its protective outermost layer.

The fact that in using a resistive ribbon heat is generated directly in the resistive ribbon and only the travelling ribbon gets hot (not the print heads) an inherent advantage in printing speed is obtained. In applying the thermal printing head technology the various elements of the thermal printing head get hot and must cool down before the head can print without cross-talk in a next position.

In a second embodiment of the method according to the present invention the recording layer of said recording material is heated image-wise or pattern-wise by means of a modulated laser beam. For example, image-wise modulated laser light is used to heat the recording layer image-wise by means of substances converting absorbed laser light, e.g. infrared radiation into heat. In said embodiment the recording layer or a layer in intimate thermo-conductive contact therewith contains light-into-heat converting substances, e.g. infrared radiation absorbing substances.

The imagewise applied laser light has not necessarily to be infrared light since the power of a laser in the visible light range and even in the ultraviolet region can be thus high that sufficient heat is generated on absorption of the laser light in the recording material. There is no limitation on the kind of laser used which may be a gas laser, gas ion laser, e.g. argon ion laser, solid state laser, e.g. Nd:YAG laser, dye laser or semi-conductor laser.

The use of an infrared light emitting laser and a dye-donor element containing an infrared light absorbing material is described e.g. in US-P 4,912,083. Suitable infra-red light absorbing dyes for laser-induced thermal dye transfer are described e.g. in US-P 4,948,777, which US-P documents for said dyes and applied lasers have to be read in conjunction herewith.

In a third embodiment the image- or pattern-wise heating of the recording material proceeds by means of pixelwise modulated ultra-sound, using e.g. an ultrasonic pixel printer as described e.g. in US-P 4,908,631.

The image signals for modulating the ultrasonic pixel printer, laser beam or electrode current are obtained directly e.g. from opto-electronic scanning devices or from an intermediary storage means, e.g. magnetic disc or tape or optical disc storage medium, optionally linked to a digital image work station wherein the image information can be processed to satisfy particular needs.

Direct thermal imaging can be used for both the production of transparencies and reflection type prints. Such means that the support will be transparent or opaque, e.g. having a white light reflecting aspect. For example, a paper base is present which may contain white light reflecting pigments, optionally also applied in an interlayer between the recording layer and said base. In case a transparent base is used, said base may be colourless or coloured, e.g. has a blue colour.

In the hard copy field recording materials on white opaque base are used, whereas in the medical diagnostic field black-imaged transparencies find wide application in inspection techniques operating with a light box.

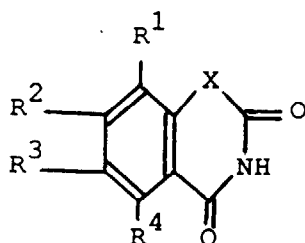
Substantially light-insensitive organic silver salts particularly suited for use according to the present invention in the heat-sensitive recording layer in admixture with the above defined polyhydroxy spiro-bis-indanes are silver salts of

aliphatic carboxylic acids known as fatty acids, wherein the aliphatic carbon chain has preferably at least 12 C-atoms, e.g. silver laurate, silver palmitate, silver stearate, silver hydroxystearate, silver oleate and silver behenate. Modified aliphatic carboxylic acids with thioether group as described e.g. in GB-P 1,111,492 and other organic silver salts as described in GB-P 1,439,478, e.g. silver benzoate and silver phthalazinone, may be used likewise to produce a thermally developable silver image. Further are mentioned silver imidazoles and the substantially light-insensitive inorganic or organic silver salt complexes described in US-P 4,260,677.

The silver image density depends on the coverage of the above defined polyhydroxy spiro-bis-indane reducing agent and organic silver salt(s) and has to be preferably such that on heating above 100 °C an optical density of at least 3 can be obtained. Preferably at least 0.10 mole of said spiro-indane reducing agent per mole of organic silver salt is used.

In order to obtain a neutral black image tone in the higher densities and neutral grey in the lower densities the recording layer contains in admixture with said organic silver salt and reducing agents a so-called toning agent known from thermography or photo-thermography.

Suitable toning agents are the phthalimides and phthalazinones within the scope of the general formulae described in the already mentioned Re. 30,107. Further reference is made to the toning agents described in US-P 3,074,809, 3,446,648 and 3,844,797. Other particularly useful toning agents are the heterocyclic toner compounds of the benzoxazine dione or naphthoxazine dione type within the scope of following general formula :



in which :

X represents O or NR⁵;

each of R¹, R², R³ and R⁴ (same or different) represents hydrogen, alkyl, e.g. C1-C20 alkyl, preferably C1-C4 alkyl, cycloalkyl, e.g. cyclopentyl or cyclohexyl, alkoxy, preferably methoxy or ethoxy, alkylthio with preferably up to 2 carbon atoms, hydroxy, dialkylamino of which the alkyl groups have preferably up to 2 carbon atoms or halogen, preferably chlorine or bromine; or R¹ and R² or R² and R³ represent the ring members required to complete a fused aromatic ring, preferably a benzene ring, or R³ and R⁴ represent the ring members required to complete a fused aromatic aromatic or cyclohexane ring. Toners within the scope of said general formula are described in GB-P 1,439,478 and US-P 3,951,660.

A toner compound particularly suited for use in combination with said polyhydroxy spiro-bis-indane reducing agents is 3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine described in US-P 3,951,660.

In addition to said ingredients the recording layer may contain other additives such as free fatty acids, surface-active agents, antistatic agents, e.g. non-ionic antistatic agents including a fluorocarbon group as e.g. in F₃C(CF₂)₆CONH(CH₂CH₂O)-H, ultraviolet light absorbing compounds, white light reflecting and/or ultraviolet radiation reflecting pigments, colloidal silica, and/or optical brightening agents.

In the recording materials according to the present invention the above ingredients are present in a polymeric binder preferably on a flexible base.

As binding agent for said ingredients preferably thermoplastic resins are used wherein the ingredients can be dispersed homogeneously or form a solid-state solution. For that purpose all kinds of natural, modified natural or synthetic resins may be used, e.g. cellulose derivatives such as ethylcellulose, cellulose esters, carboxymethylcellulose, starch ethers, galactomannan, polymers derived from α,β-ethylenically unsaturated compounds such as polyvinyl chloride, after-chlorinated polyvinyl chloride, copolymers of vinyl chloride and vinylidene chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate and partially hydrolyzed polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, e.g. polyvinyl butyral, copolymers of acrylonitrile and acrylamide, polyacrylic acid esters, polymethacrylic acid esters, polystyrene and polyethylene or mixtures thereof. A particularly suitable ecologically interesting (halogen-free) binder is polyvinyl butyral. Polyvinyl butyral containing some vinyl alcohol units is marketed under the trade name BUTVAR B79 of Monsanto USA.

The binder to organic silver salt ratio is preferably in the range of 0.2 to 6, and the thickness of the imaging, called

recording layer, is preferably in the range of 5 to 16 μm .

The above mentioned polymers or mixtures thereof forming the binder may be used in conjunction with waxes or "heat solvents" also called "thermal solvents" or "thermosolvents" improving the reaction speed of the redox-reaction at elevated temperature.

By the term "heat solvent" in this invention is meant a non-hydrolyzable organic material which is in solid state in the recording layer at temperatures below 50 °C but becomes a plasticizer for the recording layer in the heated region and/or liquid solvent for at least one of the redox-reactants, e.g. the reducing agent for the organic silver salt, at a temperature above 60 °C. Useful for that purpose are a polyethylene glycol having a mean molecular weight in the range of 1,500 to 20,000 described in US-P 3,347,675. Further are mentioned compounds such as urea, methyl sulfonamide and ethylene carbonate being heat solvents described in US-P 3,667,959, and compounds such as tetrahydrothiophene-1,1-dioxide, methyl anisate and 1,10-decanediol being described as heat solvents in Research Disclosure, December 1976, (item 15027) pages 26-28. Still other examples of heat solvents have been described in US-P 3,438,776, and 4,740,446, and in published EP-A 0 119 615 and 0 122 512 and DE-A 3 339 810.

The recording materials of the present invention are particularly suited for use in thermographic recording techniques operating with thermal print-heads. Suitable thermal printing heads are e.g. a Fujitsu Thermal Head (FTP-040 MCS001), a TDK Thermal Head F415 HH7-1089, and a Rohm Thermal Head KE 2008-F3.

In a particular embodiment in order to avoid direct contact of the printheads with the recording layer that has not been provided with an outermost protective layer, the imagewise heating of the recording layer with said printheads proceeds through a contacting but removable resin sheet or web wherefrom during said heating no transfer of imaging material can take place.

The base or support of the heat-sensitive recording material according to the present invention may be transparent, translucent or opaque and is preferably a thin flexible carrier made e.g. from paper, polyethylene coated paper or transparent resin film, e.g. made of a cellulose ester, e.g. cellulose triacetate, polypropylene, polycarbonate or polyester, e.g. polyethylene terephthalate. The support may be in sheet, ribbon or web form and subbed if need be to improve the adherence to the thereon coated heat-sensitive recording layer. The support may be made of an opacified resin composition, e.g. is made of opacified polyethylene terephthalate by means of pigments and/or micro-voids and/or is coated with an opaque pigment-binder layer, and may be called synthetic paper or paperlike film. Information about such support can be found in EP 194106, 234563 and US-P 3,944,699, 4,187,113, 4,780,402 and 5,059,579.

The coating of the heat-sensitive recording layer may proceed by any coating technique e.g. as described in Modern Coating and Drying Technology, edited by Edward D. Cohen and Edgar B. Gutoff, (1992) VCH Publishers Inc. 220 East 23rd Street, Suite 909 New York, NY 10010, U.S.A.

The following examples illustrate the present invention. The percentages and ratios are by weight unless otherwise indicated.

EXAMPLE 1 (comparative example)

A thermographic recording material according to the present invention is prepared and tested as described hereinafter.

A subbed polyethylene terephthalate support having a thickness of 100 μm was doctor blade-coated so as to obtain thereon after drying the following recording layer A including :

silver behenate	5 g/m ²
polyvinyl butyral	2.5 g/m ²
behenic acid	0.46 g/m ²
indane I	0.95 g/m ²
3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine	0.36 g/m ²
silicone oil	0.02 g/m ²

The recording layer B contained 0.61 g/m² of pyrocatechol (1,2-dihydroxybenzene), and recording layer C contained 0.61 g/m² of hydroquinone (1,4-dihydroxybenzene) instead of said indane I.

The coverage of said indane I reductor in recording layer A and of said dihydroxy-benzene reductor in said recording layers B and C was in equivalent amounts taking into account the number of hydroxyl groups present in each of said reducers.

After drying, a part (part P) of the thus coated recording materials A, B and C was kept for 3 days at 20 °C (room temperature) and relative humidity (R.H.) of 60 %, and another part (part Q) was kept for the same period at 57 °C and R.H. of 34 %.

In a first test parts P and Q of said materials A, B and C were pressed through their rear side in contact with an

aluminium bar electrically heated to obtain a temperature of 140 °C. After a contacting time of 10 s the test strips were removed and their optical density was measured. The optical density results are presented in the following Table 1.

TABLE 1

Recording material	Part	Optical density
A	P	4.5
A	Q	4.5
B	P	2.6
B	Q	0.6
C	P	3.5
C	Q	0.46

In a second test the parts P and Q of said recording materials A, B and C were used in a thermal printer MITSUBISHI CP100 (tradename) wherein the printing proceeded while having the printing head in contact with one side of a 5 µm thick polyethylene terephthalate web (blanco web), the other side being in contact with the recording layer of the above defined recording materials.

The optical densities of the imaged and non-imaged areas were measured in transmission with densitometer Macbeth TD 904 (tradename) provided with an ortho filter (maximal transmission at about 500 nm). The measured minimum ($D_{\min}$) and maximum ($D_{\max}$) optical density results are presented in the following Table 2.

TABLE 2

Recording material	Part	$D_{\min}$	$D_{\max}$
A	P	0.07	3.7
A	Q	0.09	3.6
B	P	0.08	3.3
B	Q	0.11	0.47
C	P	0.08	3.24
C	Q	0.11	0.38

The still very low minimum density in the recording layer part Q of invention material A that had been subjected to the defined thermal pre-treatment (57 °C, 34 % R.H.) proves the very good stability of the present recording layer by means of which still an optical density of almost 4 can be obtained in areas heated by said thermal printhead recorder (operating at a temperature well above 100 °C).

On the contrary in the comparison recording materials B and C said thermal pre-treatment was considerably lowering the normally obtainable maximum density and fog ($D_{\min}$) was higher.

EXAMPLE 2

A thermographic recording material according to the present invention is prepared and exposed with infrared (IR) laser beam as described hereinafter.

- Preparation of the recording material

A subbed polyethylene terephthalate support having a thickness of 100 µm was doctor blade-coated from a methyl ethylketone coating solution so as to obtain thereon after drying the following recording layer including :

silver behenate	1.65 g/m²
polyvinyl butyral	0.820 g/m²
behenic acid	0.165 g/m²
indane 1	0.300 g/m²
3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine	0.120 g/m²

component 1 (see structure hereinafter)

0.19 g/m²

component 2 (see structure hereinafter)

0.29 g/m²

Component 1 and 2 together form an infrared light absorbing complex.

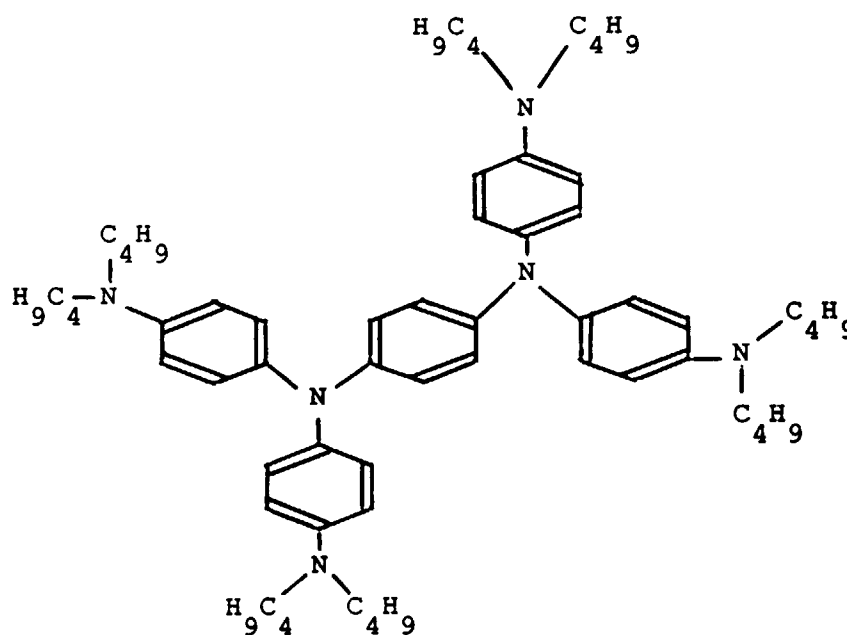
The absorption (density) of the dried layer was 0.72 at 1053 nm.

- IR laser-exposure

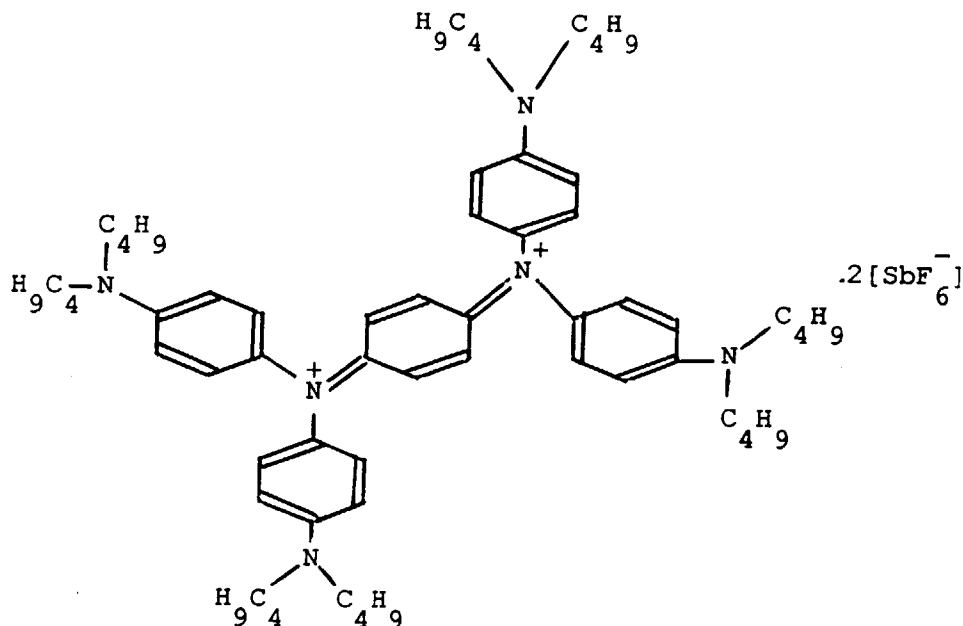
The recording material was exposed by means of a Nd-YLF (yttrium lithium fluoride) laser emitting at 1053 nm (spot diameter 18 µm; laser power striking the film : 1.60 W; writing time for A3 format : 24 min).

The optical density in the laser-exposed areas measured as in Example 1 was : 0.47.

Component 1 has the following structural formula :

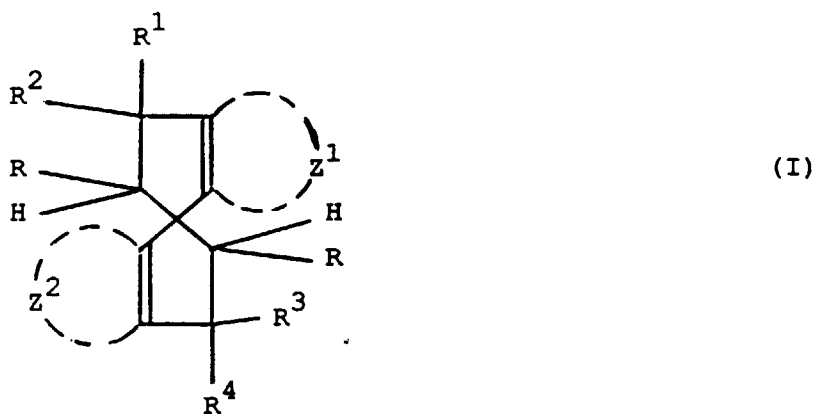


Component 2 has the following structural formula :



Claims

1. A recording material suited for use in direct thermal imaging, wherein said recording material comprises : (i) a support and (ii) at least one imaging layer containing uniformly distributed in a polymeric binder (1) a substantially light-insensitive organic silver salt in thermal working relationship with (2) at least one organic reducing agent, characterized in that said organic reducing agent is a polyhydroxy spiro-bis-indane.
2. Recording material according to claim 1, wherein said polyhydroxy spiro-bis-indane is within the scope of following formula (I):

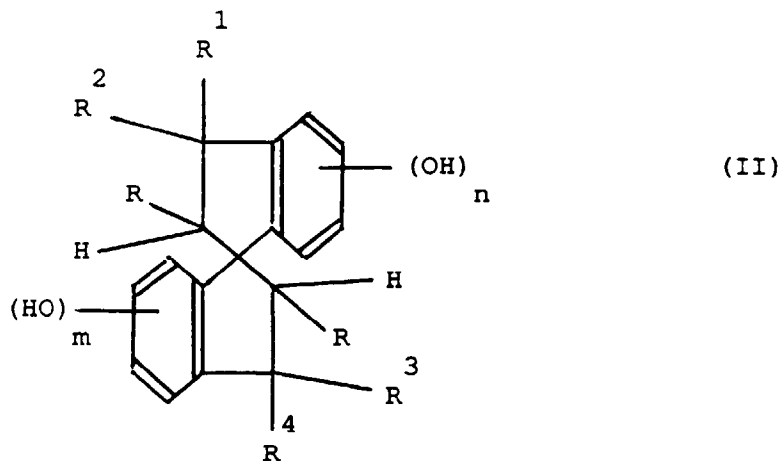


wherein :

R represents hydrogen or alkyl,
 each of R¹ and R² (same or different) represents hydrogen, an alkyl group, an alkenyl group or a cycloalkyl group, or R¹ and R² together represent the atoms necessary to close a homocyclic non-aromatic ring,
 each of R³ and R⁴ (same or different) represents hydrogen, an alkyl group, an alkenyl group or a cycloalkyl group, or R³ and R⁴ together represent the atoms necessary to close a homocyclic non-aromatic ring, and
 each of Z¹ and Z² (same or different) represents the atoms necessary to close an aromatic ring or ring system

substituted with at least two hydroxyl groups in ortho- or para-position and optionally further substituted with at least one hydrocarbon group.

3. Recording material according to claim 1 or 2, wherein said polyhydroxy spiro-bis-indane compound corresponds to the following general formula (II) :



wherein :

R represents hydrogen or alkyl,

each of R¹ and R² (same or different) represents, an alkyl group, or a cycloalkyl group,

each of R³ and R⁴ (same or different) represents, an alkyl group, or a cycloalkyl group, and

n is a positive integer 2 or 3,

m represents zero or is a positive integer 1, 2 or 3, and at least two of the hydroxyl groups of said formula are in ortho- or para-position.

4. Recording material according to claim 3, wherein said polyhydroxy spiro-bis-indane is di-methyl substituted in both of its indane rings, in the 3- and 3'-position of the spiro-bis-indane.

5. Recording material according to claim 1, wherein said polyhydroxy spiro-bis-indane is selected from the group consisting of 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-1,1'-spiro-bis-indane; 3,3,3',3'-tetramethyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indane; 1,1'-spirobi[1H-indene]-4,5,5',6,6',7'-hexol; 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl; 1,1'-spirobi[indan]-5,5',6,6'-tetrol; 3-methyl-3-ethyl, 3'-methyl-3'-ethyl; 1,1'-spirobi[indan]-5,5',6,6'-tetrol, 2-ethyl-3,3-dimethyl-3,3'-dipropyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol; 3,3'-diethyl-2,2',3,3'-tetrahydro-2,3,3'-trimethyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol; 2,2'-diethyl-2,2',3,3'-tetrahydro-3,3,3',3'-tetrapropyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol; 3,3'-diethyl-2,2',3,3'-tetrahydro-2,2',3,3'-tetramethyl; 1,1'-spirobi[1H-indene]-4,4',5,5',6,6'-hexol; 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl; 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol; 3,3'-diethyl-2,2',3,3'-tetrahydro-3,3'-dimethyl; 1,1'-spirobi[1H-indene]-5,5',6,6',7,7'-hexol; 2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl; and 1,1'-spirobi[1H-indene]-5,5',6,6'-tetrol; 2,2',3,3'-tetrahydro-3,3,3',3',7,7'-hexamethyl.

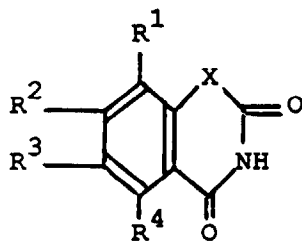
6. Recording material according to any of claims 1 to 5, wherein said substantially light-insensitive organic silver salt is a silver salt of an aliphatic carboxylic acid (fatty acid) having at least 12 C-atoms.

7. Recording material according to claim 6, wherein said organic silver salt is silver palmitate, silver stearate or silver behenate or mixtures thereof.

8. Recording material according to any of claims 1 to 7, wherein the coverage of said spiro-bis-indane reducing agent and organic silver salt(s) is such that on heating the recording material above 100 °C an optical density of at least 3 can be obtained.

9. Recording material according to any of claims 1 to 8, wherein at least 0.10 mole of said polyhydroxy spiro-bis-indane compound is present per mole of organic silver salt.

10. Recording material according to any of claims 1 to 9, wherein the recording layer contains in admixture with said polyhydroxy spiro-bis-indane at least one toning agent being a phthalimide, phthalazinone or heterocyclic compound corresponding to the following general formula :



in which :

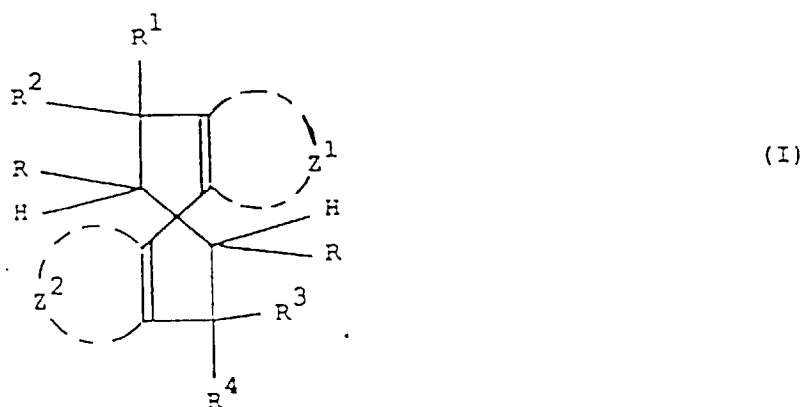
X represents O or NR⁵;

each of R¹, R², R³ and R⁴ (same or different) represents hydrogen, alkyl, cycloalkyl, alkoxy, alkylthio, hydroxy, dialkylamino or halogen; or R¹ and R² or R² and R³ represent the ring members required to complete a fused aromatic ring, or R³ and R⁴ represent the ring members required to complete a fused aromatic or cyclohexane ring.

11. Recording material according to any of claims 1 to 10, wherein said binder is a polyvinylbutyral.
12. Recording material according to any of claims 1 to 11, wherein said recording layer contains additives selected from the group consisting of surface-active agents, antistatic agents, ultraviolet light absorbing compounds, white light reflecting and/or ultraviolet radiation reflecting pigments, colloidal silica, and/or optical brightening agents.
13. Recording material according to any of claims 1 to 12, wherein said substantially light-insensitive organic silver salt and said organic reducing agent are present in admixture in the same layer containing said polymeric binder.
14. Recording material according to any of claims 1 to 12, wherein said substantially light-insensitive organic silver salt and said organic reducing agent are present in different layers wherefrom by heat they can come into reactive contact with each other.
15. A recording process wherein a recording material according to any of the above claims 1 to 14 is exposed to a heat pattern in direct thermal imaging, by which is meant that during the application of said heat pattern a visible image is formed in said recording material without the aid of substances that are thermally pattern-wise transferred thereon and/or therein.
16. Recording process according to claim 15, wherein the pattern-wise heating of the recording material proceeds by Joule effect heating in that selectively energized electrical resistors of a thermal head array are used in contact or close proximity with the recording layer of said recording material.
17. Recording process according to claim 15, wherein the pattern-wise heating proceeds electrically by means of an electrically resistive ribbon.
18. Recording process according to claim 15, wherein the pattern-wise heating of the recording layer proceeds by means of a modulated laser beam.
19. Recording process according to claim 18, wherein said heating proceeds by means of substances converting absorbed laser light into heat.
20. Recording process according to claim 15, wherein the pattern-wise heating of said recording material proceeds by means of pixelwise modulated ultra-sound.

Patentansprüche

- Ein zur Verwendung in der thermischen Direktbilderzeugung geeignetes Aufzeichnungsmaterial, das die folgenden Bestandteile enthält : (i) einen Träger und (ii) wenigstens eine Bilderzeugungsschicht, die gleichmäßig in einem polymeren Bindemittel verteilt (1) ein wesentlich lichtunempfindliches organisches Silbersalz in thermisch wirksamer Beziehung mit (2) wenigstens einem organischen Reduktionsmittel enthält, dadurch gekennzeichnet, daß das organische Reduktionsmittel ein Polyhydroxyspiro-bis-indan ist.
- Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Polyhydroxyspiro-bis-indan der nachstehenden Formel (I) entspricht :



in der bedeuten :

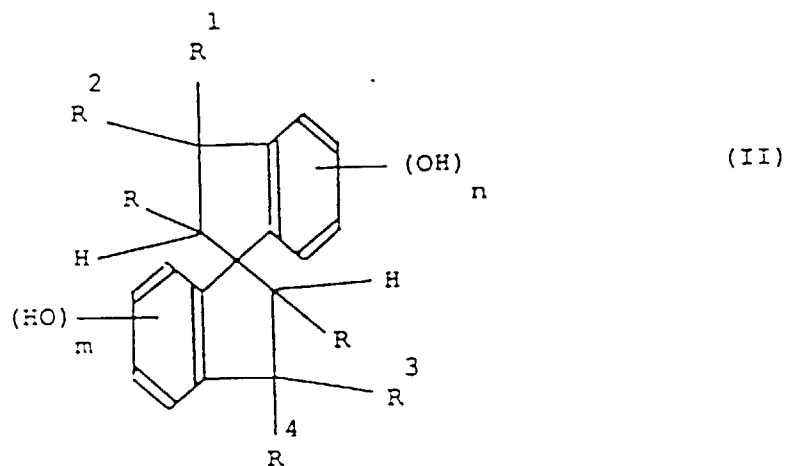
R Wasserstoff oder eine Alkylgruppe,

R¹ und R² (gleich oder verschieden) je Wasserstoff, eine Alkylgruppe, eine Alkenylgruppe oder eine Cycloalkylgruppe, oder R¹ und R² zusammen die zum Schließen eines homocyclischen nicht-aromatischen Ringes benötigten Atome,

R³ und R⁴ (gleich oder verschieden) je Wasserstoff, eine Alkylgruppe, eine Alkenylgruppe oder eine Cycloalkylgruppe, oder R³ und R⁴ zusammen die zum Schließen eines homocyclischen nicht-aromatischen Ringes benötigten Atome,

Z¹ und Z² (gleich oder verschieden) je die zum Schließen eines aromatischen, mit wenigstens zwei Hydroxylgruppen an der ortho- oder para-Stellung und weiterhin gegebenenfalls mit wenigstens einer Kohlenwasserstoffgruppe substituierten Ringes oder Ringsystems benötigten Atome.

- Aufzeichnungsmaterial nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polyhydroxyspiro-bis-indan der nachstehenden allgemeinen Formel (II) entspricht :



in der bedeuten :

R Wasserstoff oder eine Alkylgruppe,

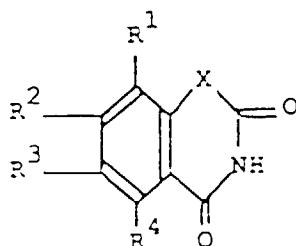
R¹ und R² (gleich oder verschieden) je Wasserstoff, eine Alkylgruppe oder eine Cycloalkylgruppe,

R³ und R⁴ (gleich oder verschieden) je Wasserstoff, eine Alkylgruppe oder eine Cycloalkylgruppe,

n eine positive ganze Zahl 2 oder 3,

m Null oder eine positive ganze Zahl 1, 2 oder 3, und in der sich wenigstens zwei der Hydroxylgruppen der Formel an ortho- oder para-Stellung befinden.

4. Aufzeichnungsmaterial nach Anspruch 3, dadurch gekennzeichnet, daß das Polyhydroxyspiro-bis-indan in seinen beiden Indanringen, an der 3- und 3'-Stellung des Spiro-bis-indans mit einer Dimethylgruppe substituiert ist.
5. Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Polyhydroxyspiro-bis-indan aus der nachstehenden Gruppe gewählt wird : 3,3,3',3'-Tetramethyl-5,6,5',6'-tetrahydroxy-1,1'-spiro-bis-indan, 3,3,3',3'-Tetramethyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indan, 1,1'-Spirobi[1H-inden]-4,5,5',6,6',7'-hexol, 2,2',3,3'-Tetrahydro-3,3,3',3'-tetramethyl, 1,1'-Spirobi[indan]-5,5',6,6'-tetrol, 3-Methyl-3-ethyl, 3'-Methyl-3'-ethyl, 1,1'-Spirobi[indan]-5,5',6,6'-tetrol, 2-Ethyl-3,3-dimethyl-3,3'-dipropyl, 1,1'-Spirobi[1H-inden]-5,5',6,6'-tetrol, 3,3'-Diethyl-2,2',3,3'-tetrahydro-2,3,3'-trimethyl, 1,1'-Spirobi[1H-inden]-5,5',6,6'-tetrol, 2,2'-Diethyl-2,2',3,3'-tetrahydro-3,3,3',3'-tetrapropyl, 1,1'-Spirobi[1H-inden]-5,5',6,6'-tetrol, 3,3'-Diethyl-2,2',3,3'-tetrahydro-2,2',3,3'-tetramethyl, 1,1'-Spirobi[1H-inden]-4,4',5,5',6,6'-hexol, 2,2',3,3'-Tetrahydro-3,3,3',3'-tetramethyl, 1,1'-Spirobi[1H-inden]-5,5',6,6'-tetrol, 3,3'-Diethyl-2,2',3,3'-tetrahydro-3,3'-dimethyl, 1,1'-Spirobi[1H-inden]-5,5',6,6',7,7'-hexol, 2,2',3,3'-Tetrahydro-3,3,3',3'-tetramethyl, 1,1'-Spirobi[1H-inden]-5,5',6,6'-tetrol und 2,2',3,3'-Tetrahydro-3,3,3',3',7,7'-hexamethyl.
6. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das wesentlich lichtunempfindliche organische Silbersalz ein Silbersalz einer aliphatischen Carbonsäure (Fettsäure) mit wenigstens 12 Kohlenstoffatomen ist.
7. Aufzeichnungsmaterial nach Anspruch 6, dadurch gekennzeichnet, daß das organische Silbersalz Silberpalmitat, Silberstearat oder Silberbehenat oder Mischungen derselben ist.
8. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Auftrag des Spiro-bis-indan-Reduktionsmittels und des (der) organischen Silbersalze(s) derart gewählt wird, daß bei der Erhitzung des Aufzeichnungsmaterials oberhalb 100°C eine optische Densität von wenigstens 3 erzielt werden kann.
9. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß pro Mol organisches Silbersalz wenigstens 0,10 Mol Polyhydroxyspiro-bis-indan-Reduktionsmittel enthalten ist.
10. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die Aufzeichnungsschicht in Beimischung mit dem Polyhydroxyspiro-bis-indan wenigstens ein Tönungsmittel enthält, nämlich ein Phthalimid, ein Phthalazinon oder eine heterocyclische Verbindung nach der folgenden allgemeinen Formel :



in der bedeuten :

X O oder NR⁵,

R¹, R², R³ und R⁴ (gleich oder verschieden) je Wasserstoff, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Alkylthiogruppe, eine Hydroxylgruppe, eine Dialkylaminogruppe oder Halogen, oder R¹ und R² oder R² und R³ die zum Vervollständigen eines anellierten aromatischen Ringes benötigten Ringglieder, oder R³ und R⁴ die zum Vervollständigen eines anellierten aromatischen Ringes oder Cyclohexanringes

benötigten Ringglieder.

11. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß das Bindemittel ein Polyvinylbutyral ist.

12. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß die Aufzeichnungsschicht andere Zusatzstoffe enthält wie oberflächenaktive Mittel, Antistatikmittel, Ultraviolettlicht absorbierende Verbindungen, Weißlicht reflektierende und/oder Ultraviolettstrahlung reflektierende Pigmente, kolloidale Kiesel-erde und/oder Weißtöner.

13. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß das wesentlich lichtunempfindliche organische Silbersalz und das organische Reduktionsmittel derselben das polymere Bindemittel enthaltenden Schicht beigemischt sind.

14. Aufzeichnungsmaterial nach irgendeinem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß das wesentlich lichtunempfindliche organische Silbersalz und das organische Reduktionsmittel verschiedenen Schichten beigemischt sind, aus denen sie durch Wärme in reaktive Berührung miteinander treten können.

15. Ein Aufzeichnungsverfahren, in dem ein Aufzeichnungsmaterial nach irgendeinem der vorstehenden Ansprüche 1 bis 14 in der thermischen Direktbilderzeugung an einem Wärmemuster belichtet wird, was bedeutet, daß sich beim Anbringen des Wärmemusters im Aufzeichnungsmaterial ein sichtbares Bild bildet, ohne daß die thermisch mustermäßig darauf und darin übertragenen Substanzen dazu wirksam beitragen.

16. Aufzeichnungsverfahren nach Anspruch 15, dadurch gekennzeichnet, daß die mustermäßige Erhitzung des Aufzeichnungsmaterials durch Joule-Effekt-Erhitzung erfolgt, wobei selektiv erregte elektrische Widerstände einer Druckkopfmatrix in Kontakt mit oder in nächster Nähe von der Aufzeichnungsschicht des Aufzeichnungsmaterials benutzt werden.

17. Aufzeichnungsverfahren nach Anspruch 15, dadurch gekennzeichnet, daß die mustermäßige Erhitzung elektrisch mittels eines elektrisch beständigen Bandes erfolgt.

18. Aufzeichnungsverfahren nach Anspruch 15, dadurch gekennzeichnet, daß die mustermäßige Erhitzung der Aufzeichnungsschicht mittels eines modulierten Laserstrahlenbündels erfolgt.

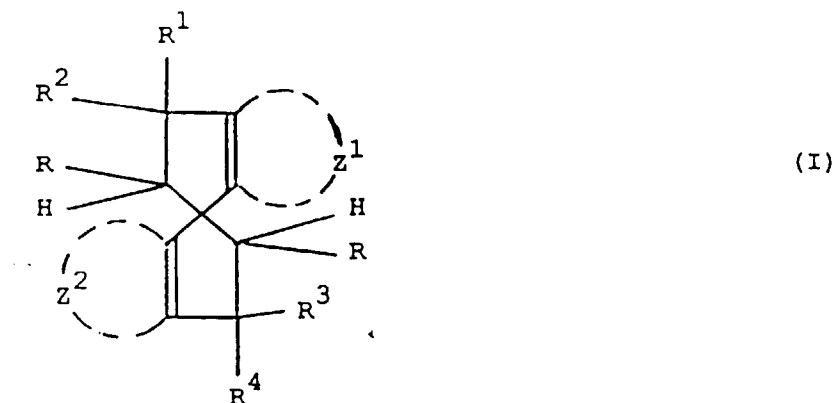
19. Aufzeichnungsverfahren nach Anspruch 18, dadurch gekennzeichnet, daß die Erhitzung mit Licht-in-Wärme umwandelnden Substanzen erfolgt.

20. Aufzeichnungsverfahren nach Anspruch 15, dadurch gekennzeichnet, daß die mustermäßige Erhitzung des Aufzeichnungsmaterials durch pixelweise modulierten Ultraschall erfolgt.

Revendications

1. Un matériau enregistreur approprié à être utilisé dans l'imagerie thermique directe, lequel matériau enregistreur comprend: (i) un support et (ii) au moins une couche formatrice d'image contenant, distribués de manière uniforme dans un liant polymère, (1) un sel d'argent organique essentiellement insensible à la lumière dans une relation fonctionnelle thermique avec (2) au moins un agent réducteur organique, caractérisé en ce que l'agent réducteur organique est un polyhydroxy spiro-bis-indane.

2. Matériau enregistreur selon la revendication 1, caractérisé en ce que le polyhydroxy spiro-bis-indane se situe dans la portée de la formule suivante (I):



dans laquelle:

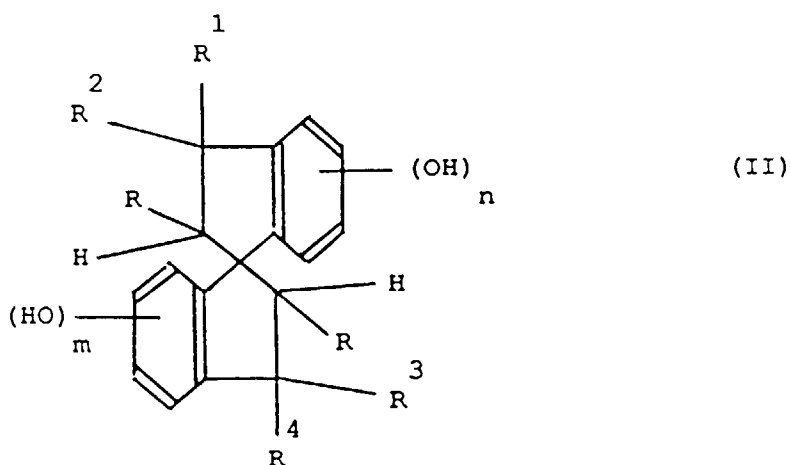
R représente un atome d'hydrogène ou un groupe alkyle,

R¹ et R² (identiques ou différents) représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe alcényle ou un groupe cycloalkyle, ou R¹ et R² ensemble représentent les atomes nécessaires pour fermer un noyau homocyclique non aromatique,

R³ et R⁴ (identiques ou différents) représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe alcényle ou un groupe cycloalkyle, ou R³ et R⁴ ensemble représentent les atomes nécessaires pour fermer un noyau homocyclique non aromatique, et

Z¹ et Z² (identiques ou différents) représentent chacun les atomes nécessaires pour fermer un noyau aromatique ou un système à noyau aromatique substitué avec au moins deux groupes hydroxyles en position ortho ou para et éventuellement substitué davantage avec au moins un groupe hydrocarbure.

3. Matériau enregistreur selon la revendication 1 ou 2, caractérisé en ce que le composé de polyhydroxy spiro-bis-indane correspond à la formule générale suivante (II):



dans laquelle:

R représente un atome d'hydrogène ou un groupe alkyle,

R¹ et R² (identiques ou différents) représentent chacun un groupe alkyle ou un groupe cycloalkyle,

R³ et R⁴ (identiques ou différents) représentent chacun un groupe alkyle ou un groupe cycloalkyle, et

n est 2 ou 3,

m est zéro ou 1, 2 ou 3, et au moins deux des groupes hydroxyles de la formule sont en position ortho ou para.

4. Matériau enregistreur selon la revendication 3, caractérisé en ce que le polyhydroxy spiro-bis-indane est substitué par un groupe diméthylque dans ses deux noyaux indane, en position 3 et 3' du spiro-bis-indane.

5. Matériau enregistreur selon la revendication 1, caractérisé en ce que le polyhydroxy spiro-bis-indane est choisi du groupe se composant de:

3,3,3',3'-tétraméthyl-5,6,5',6'-tétrahydroxy-1,1'-spiro-bis-indane; 3,3,3',3'-tétraméthyl-4,6,7,4',6',7'-hexahydroxy-1,1'-spiro-bis-indane; 1,1'-spirobi[[H-indène]-4,5,5',6,6',7'-hexol, 2,2',3,3'-tétrahydro-3,3,3',3'-tétraméthyle; 1,1'-spirobi[indane]-5,5',6,6'-tétrole, 3-méthyl-3-éthyle, 3'-méthyl-3'-éthyle; 1,1'-spirobi[indane]-5,5',6,6'-tétrole, 2-éthyl-3,3-diméthyl-3,3'-dipropyle; 1,1'-spirobi[[H-indène]-5,5',6,6'-tétrole, 3,3'-diéthyl-2,2',3,3'-tétrahydro-2,3,3'-triméthyle; 1,1'-spirobi[1H-indène]-5,5',6,6'-tétrole, 2,2'-diéthyl-2,2',3,3'-tétrahydro-3,3,3',3'-tétrapropyle; 1,1'-spirobi[1H-indène]-5,5',6,6'-tétrole, 3,3'-diéthyl-2,2',3,3'-tétrahydro-2,2',3,3'-tétraméthyle; 1,1'-spirobi[1H-indène]-4,4',5,5',6,6'-hexol, 2,2',3,3'-tétrahydro-3,3,3',3'-tétraméthyle; 1,1'-spirobi[1H-indène]-5,5',6,6'-tétrole, 3,3'-diéthyl-2,2',3,3'-tétrahydro-3,3'-diméthyle; 1,1'-spirobi[[H-indène]-5,5',6,6',7'-hexol, 2,2',3,3'-tétrahydro-3,3,3',3'-tétraméthyle; et 1,1'-spirobi[1H-indène]-5,5',6,6'-tétrole, 2,2',3,3'-tétrahydro-3,3,3',7,7'-hexaméthyle.

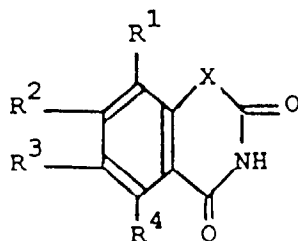
6. Matériau enregistreur selon l'une quelconque des revendications 1 à 5, caractérisé en ce que le sel d'argent organique essentiellement insensible à la lumière est un sel d'argent d'un acide carboxylique aliphatique (acide gras) ayant au moins 12 atomes de carbone.

7. Matériau enregistreur selon la revendication 6, caractérisé en ce que le sel d'argent organique et le palmitate d'argent, le stéarate d'argent ou le béhénate d'argent ou des mélanges de ceux-ci.

8. Matériau enregistreur selon l'une quelconque des revendications 1 à 7, caractérisé en ce que le taux d'application de l'agent réducteur de spiro-bis-indane et du (des) sel(s) d'argent organique(s) est tel qu'en échauffant le matériau enregistreur au-dessus de 100 °C on peut obtenir une densité optique d'au moins 3.

9. Matériau enregistreur selon l'une quelconque des revendications 1 à 8, caractérisé en ce qu'au moins 0,10 mole du composé de polyhydroxy spiro-bis-indane est présent par mole de sel d'argent organique.

10. Matériau enregistreur selon l'une quelconque des revendications 1 à 9, caractérisé en ce que la couche enregistreuse contient, en mélange avec le polyhydroxy spiro-bis-indane, au moins un agent influençant le ton d'image qui est un phtalimide, une phtalazinone ou un composé hétérocyclique correspondant à la formule générale suivante:



dans laquelle:

X représente O ou NR⁵;

R¹, R², R³ et R⁴ (identiques ou différents) représentent un atome d'hydrogène, un groupe alkyle, un groupe cycloalkyle, un groupe alkoxy, un groupe alkylthio, un groupe hydroxy, un groupe dialkylamino ou un atome d'halogène; ou R¹ et R² ou R² et R³ représentent les membres de noyau nécessaires pour compléter un noyau aromatique condensé, ou R³ et R⁴ représentent les membres de noyau nécessaires pour compléter un noyau aromatique ou cyclohexane condensé.

11. Matériau enregistreur selon l'une quelconque des revendications 1 à 10, caractérisé en ce que le liant est le polyvinylbutyral.

12. Matériau enregistreur selon l'une quelconque des revendications 1 à 11, caractérisé en ce que la couche enregistreuse contient des additifs choisis dans le groupe se composant d'agents tensioactifs, d'agents antistatiques, de composés absorbant la lumière ultraviolette, de pigments réfléchissant la lumière blanche et/ou réfléchissant le rayonnement ultraviolet, de silice colloïdale et/ou d'aviveurs optiques.

13. Matériau enregistreur selon l'une quelconque des revendications 1 à 12, caractérisé en ce que le sel d'argent organique essentiellement insensible à la lumière et l'agent réducteur organique sont présents mélangés dans la même couche contenant le liant polymère.

5 **14.** Matériau enregistreur selon l'une quelconque des revendications 1 à 12, caractérisé en ce que le sel d'argent organique essentiellement insensible à la lumière et l'agent réducteur organique sont présents dans des couches différentes à partir desquelles ils peuvent se mettre en contact réactif par l'action de la chaleur.

10 **15.** Un procédé enregistreur, caractérisé en ce qu'un matériau enregistreur selon l'une quelconque des revendications précédentes 1 à 14 est exposé à un modèle thermique dans l'imagerie thermique directe, ce qui veut dire que pendant l'application de ce modèle thermique il se forme une image visible dans ce matériau enregistreur sans l'aide de substances qui sont thermiquement transférées là-dessus et/ou là-dedans sous forme de modèle.

15 **16.** Procédé enregistreur selon la revendication 15, caractérisé en ce que l'échauffement sous forme de modèle du matériau enregistreur s'effectue par l'échauffement à effet Joule par le fait que des résistances électriques sélectivement excitées d'un arrangement de tête thermique sont utilisées en contact ou en proximité immédiate avec la couche enregistreuse du matériau enregistreur.

20 **17.** Procédé enregistreur selon la revendication 15, caractérisé en ce que l'échauffement sous forme de modèle s'effectue de façon électrique au moyen d'un ruban électrorésistant.

18. Procédé enregistreur selon la revendication 15, caractérisé en ce que l'échauffement sous forme de modèle de la couche enregistreuse s'effectue au moyen d'un rayon laser modulé.

25 **19.** Procédé enregistreur selon la revendication 18, caractérisé en ce que cet échauffement s'effectue au moyen de substances transformant la lumière laser absorbée en chaleur.

30 **20.** Procédé enregistreur selon la revendication 15, caractérisé en ce que l'échauffement sous forme de modèle du matériau enregistreur s'effectue au moyen d'ultrason modulé sous forme de pixels.

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