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(54) DIRECT THERMAL IMAGING MATERIAL

WÄRMEEMPFINDLICHES AUFZEICHNUNGSMATERIAL

PRODUIT POUR UNE THERMOGRAPHIE DIRECTE

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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. More in particular the present invention relates to a recording material based on a heat induced reaction between a substantially light insensitive organic silver salt and a reducing agent.

2. Background of the Invention

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 of 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.

US 3.031.329 discloses a recording material comprising on a support a heat-sensitive layer comprising a substantially light-insensitive organic silver salt and a reducing agent. The heat-sensitive layer may be coated with a protective layer.

High optical densities can be obtained using a recording material comprising on a support a heat sensitive layer comprising a substantially light insensitive organic silver salt and a reducing agent. Such material can be image-wise heated using a thermal head causing a reaction between the reducing agent and the substantially light insensitive organic silver salt leading to the formation of metallic silver. To obtain a good thermosensitivity heating is carried out by contacting the thermal head with the heat sensitive layer. The density level may be controlled by varying the amount of heat applied to the recording material. This is generally accomplished by controlling the number of heat pulses generated by the thermal head. An image having a grey scale is thus obtained.

Because of its high density the image is in principal suitable for use as a medical diagnostic image. However the following problems have been encounterred. Uneveness of density occurs with the number of images that have been printed and damaging of the heat sensitive layer occurs. These problems can be overcome by making use of a protective layer. Although this brings a substantial improvement so that the image may be suitable for some applications, the images show scratches and artifacts.

3. Summary of the invention.

It is an object of the present invention to improve the quality of images obtained by direct thermal imaging of a recording material comprising on a support (i) a heat sensitive layer comprising a substantially light insensitive organic silver salt and (ii) a reducing agent being present in the heat sensitive layer or another layer on the same side of the support carrying the heat sensitive layer.

Further objects of the present invention will become clear from the description hereinafter.

According to the present invention there is provided a recording material comprising on a support (i) a heat sensitive layer comprising a substantially light insensitive organic silver salt, (ii) a protective layer containing a thermomeltable particle dispersed in a binder and (iii) a reducing agent being present in the heat sensitive layer and/or another layer on the same side of the support carrying the heat sensitive layer.

According to the present invention there is provided a method for making an image comprising image-wise heating by means of a thermal head a recording material as defined above said thermal head contacting the protective layer of said recording material.

4. Detailed description

Thanks to the use of thermomeltable particles in the protective layer the occurrences of artifacts in the image can be overcome and the occurrences of scratches can be reduced. Because of the high quality of the obtained images they may be used in medical diagnostics.

The thermomeltable particles for use in connection with the present invention are particles that are solid at room temperature but that easily melt at the temperatures used in the heating process that are typically around 400°C. Generally they will have a melting temperature of at least 50°C more preferably at least 150°C. Typical examples of thermomeltable particles in connection with the present invention are waxes such as e.g. amide waxes, bees wax, polyethylene wax, polytetrafluoroethylene wax, Carnauba wax etc... The particle size of the thermomeltable particles is preferably between 1μm and 10μm more preferably between 2μm and 8μm. They are preferably added to the protective layer in an amount of 0.1% to 10% by weight of the binder in the protective layer. Too low amounts will generally not provide the desired effect, whereas too large amounts of the thermomeltable particles may disturb the visual appearance of the image.

In order to reduce the scratches that sometimes occur in the image it is preferred to also add a matting agent to the protective layer. Suitable matting agents for use in connection with the present invention can be organic or inorganic. They should be sufficiently large to avoid the scratches but are on the other hand limited in their size because of pinholes that may occur at places where a matting agent is present due to a reduced thermosensitivity at these places. Preferably the matting agent will have an average diameter between 0.7 and 1.5 times the thickness of the protective layer. It is also preferred that the matting agents for use in connection with the present invention are capable of withstanding the temperatures involved in the heating process according to the present invention. Generally they should be able to withstand a temperature of up to 400°C without showing substantial deformations. The matting agent is preferably spherical in shape.

Examples of matting agents that can be used are silicone resin particles, silica, alumina, polymethylmethacrylate particles, polyacrylate particles etc...

The binder for use in the protective layer in connection with the present invention is preferably polymeric and can be selected from amongst hydrophobic and hydrophilic binders. The latter are preferred in connection with the present invention since it has been found that less dirt forms on the thermal head during printing. The protective layer may also be hardened. Hardening may be carried out by means of UV or electron beam curing or the hardening may be effected using a chemical reaction between a hardening agent and the binder. Suitable hardening agents that can be used to harden a binder having active hydrogens are e.g. polyisocyanates, aldehydes and hydrolysed tetraalkyl orthosilicates.

Examples of binders that can be used in connection with the present invention are e.g. copolymers of styrene and acrylonitrile, copolymers of styrene, acrylonitrile and butadiene, nitrocellulose, copolymers of vinylacetate and vinylchloride which may be partially hydrolysed, polyesters and polycarbonates.

Suitable hydrophilic binders for use in connection with the present invention include polyvinyl alcohol, polyvinyl acetate preferably hydrolysed in amount of 20% by weight or more, polyvinylpyrrolidone, gelatine etc... The hydrophilic binder for use in the protective layer preferably has a weight average molecular weight of at least 20000 g/mol more preferably at least 30000 g/mol. According to a most preferred embodiment in connection with the present invention there is used a protective layer that contains a hydrolysed polyvinyl acetate hardened with a tetraalkyl orthosilicate.

In accordance with the present invention it is also preferred to add a lubricant to the protective layer or applying a lubricant on top of the protective layer. By using a lubricant transportation problems of the recording material under the thermal head can be avoided as well as image deformations. The lubricant is preferably used in an amount of 0.1% by weight to 10 % by weight of the binder in the protective layer. Suitable lubricants for use in connection with the present invention are e.g. silicone oils, polysiloxane-polyether copolymers, synthetic oils, saturated hydrocarbons, glycols, fatty acids and salts or esters thereof such as e.g. stearic acid, the zinc salt of stearic acid, methyl ester of stearic acid etc...

According to a particular embodiment in connection with the present invention the lubricant may be hardened together with the binder of the protective layer. For example a binder having active hydrogens and a polysiloxane having active hydrogens may be hardened by means of e.g. polyisocyanate or a tetraalkyl orthosilicate yielding a hardened protective layer containing a lubricant.

The thickness of the protective layer in connection with the present invention is preferably between 1μm and 10μm, more preferably between 1.5μm and 7μm.

Substantially light-insensitive organic silver salts particularly suited for use according to the present invention 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, and likewise silver dodecyl sulphonate described in US-P 4,504,575 and silver di-(2-ethylhexyl)-sulfosuccinate described in published European patent application 227 141. Useful modified aliphatic carboxylic acids with thioether group are described e.g. in GB-P 1,111,492 and other organic silver salts are described in GB-P 1,439,478, e.g. silver benzoate and silver phthalazinone, which may be used likewise to produce a thermally developable silver image. Further are

mentioned silver imidazolates and the substantially light-insensitive organic silver salt complexes described in US-P 4,260,677.

As binding agent for the heat sensitive layer preferably thermoplastic water insoluble resins are used wherein the ingredients can be dispersed homogeneously or form therewith 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, 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 and polyethylene or mixtures thereof. A particularly suitable ecologically interesting (halogen-free) binder is polyvinyl butyral. A polyvinyl butyral containing some vinyl alcohol units is marketed under the trade name BUTVAR™ B79 of Monsanto USA.

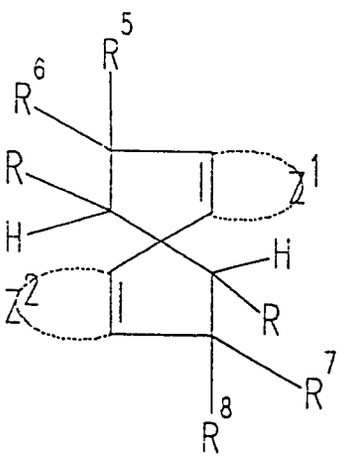
The binder to organic silver salt weight ratio is preferably in the range of 0.2 to 6, and the thickness of the image forming layer is preferably in the range of 5 to 16 μm.

The above mentioned polymers or mixtures thereof forming the binder of the heat sensitive layer may be used in conjunction with waxes or "heat solvents" also called "thermal solvents" or "thermosolvents" improving the penetration of the reducing agent(s) and thereby 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 at temperatures below 50 °C but becomes on heating above that temperature a plasticizer for the binder of the layer wherein they are incorporated and possibly act then also as a solvent for at least one of the redox-reactants, e.g. the reducing agent for the organic silver salt. 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.

Suitable organic reducing agents for the reduction of substantially light-insensitive organic silver salts are organic compounds containing at least one active hydrogen atom linked to O, N or C, such as is the case in aromatic di- and trihydroxy compounds, e.g. hydroquinone and substituted hydroquinones, catechol, pyrogallol, gallic acid and gallates; aminophenols, METOL™ p-phenylenediamines, alkoxynaphthols, e.g. 4-methoxy-1-naphthol described in US-P 3,094,417, pyrazolidin-3-one type reducing agents, e.g. PHENIDONE™, pyrazolin-5-ones, indanedione-1,3 derivatives, hydroxytetrone acids, hydroxytetronimides, reductones, and ascorbic acid. Representatives for thermally activated reduction of organic silver salts are described e.g. in US-P 3,074,809, 3,080,254, 3,094,417, 3,887,378 and 4,082,901.

Particularly suited organic reducing agents for use in thermally activated reduction of the substantially light insensitive silver salts are organic compounds containing in their structure two free hydroxy groups (-OH) in ortho-position on a benzene nucleus as is the case in catechol and polyhydroxy spiro-bis-indane compounds corresponding to the following general formula (I) which are preferred for use in the recording material according to the present invention:



(I)

wherein :

R represents hydrogen or alkyl, e.g. methyl or ethyl,

each of R^5 and R^6 (same or different) represents, an alkyl group, preferably methyl group or a cycloalkyl group, e.g. cyclohexyl group,

each of R^7 and R^8 (same or different) represents, an alkyl group, preferably methyl group or a cycloalkyl group, e.g. cyclohexyl group, and

each of Z^1 and Z^2 (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.

Particularly useful 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.

Preferably the reducing agent is added to the heat sensitive layer but all or part of the reducing agent may be added to one or more other layers on the same side of the support as the heat sensitive layer. For example, all or part of the reducing agent may be added to the protective surface layer.

The recording material may contain auxiliary reducing agents having poor reducing power in addition to the main reducing agent described above preferably in the heat sensitive layer containing the organic silver salt. For that purpose preferably sterically hindered phenols are used.

Sterically hindered phenols as described e.g. in US-P 4,001,026 are examples of such auxiliary reducing agents that can be used in admixture with said organic silver salts without premature reduction reaction and fog-formation at room temperature.

For obtaining a neutral black image tone with silver formed in the higher optical density parts and neutral grey in the lower densities the reducible silver salt(s) and reducing agents are advantageously used in conjunction with 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 US-P 4,082,901. Further reference is made to the toning agents described in US-P 3,074,809, 3,446,648 and 3,844,797. Particularly useful toning agents are likewise the heterocyclic toner compounds of the benzoxazine dione or naphthoxazine dione type.

According to the present invention an image can be obtained with the above described recording material by image-wise heating the recording material by moving the recording material under a thermal head, said thermal head contacting the protective layer. The recording material may be heated with a temperature of upto 400°C by varying the number of heat pulses given by the thermal head. By varying the number of heat pulses the density of the corresponding image pixel is varied correspondingly.

The present invention will now be illustrated by the following examples without however the intention to limit the invention thereto. All parts are by weight unless otherwise specified.

EXAMPLE 1

Preparation of the recording materials:

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

silver behenate	4.42 g/m^2
polyvinyl butyral	4.42 g/m^2
reducing agent S as defined hereinafter	0.84 g/m^2
3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine	0.34 g/m^2
silicone oil	0.02 g/m^2

Reducing agent S is 1,1'-spirobi(1H-indene)-5,5',6,6'-tetrol-2,2',3,3'-tetrahydro-3,3,3',3'-tetramethyl.

To the heat sensitive layer was coated a protective layer having the following composition:

polycarbonate (see below)	3.5g/m^2
thermomeltable particle (see table 1)	0.175g/m^2
Tegoglide 410*™	0.175g/m^2

(*) Tegoglide 410™ is a lubricant of the polysiloxane-polyether type.

The polycarbonate used was a polycarbonate having the following recurring units:

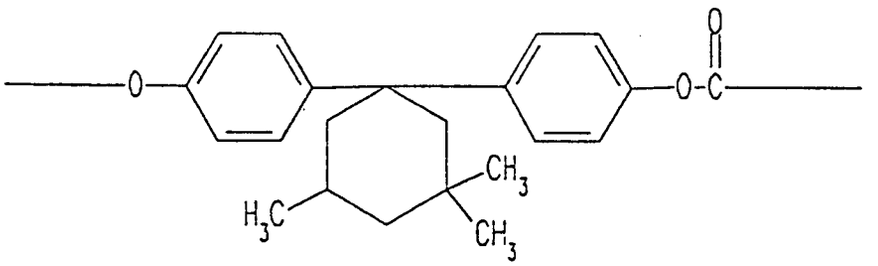


Table 1

Thermomeltable particle		
Sample no.	Type	Diameter (μm)
1	-	-
2	Lanco Wax™ HM166	3-5
3	Ceridust™ 3910	4-5
4	SST-4™	4
Lanco Wax™ is an amide wax (melting point: 185°C) obtained from Langer & Co. (Germany) Ceridust 3910 (obtained from Hoechst) is an amide wax (melting point: 141°C) corresponding to the following formula: $C_{17}H_{35}$-CONH-CH_2-CH_2-NHOC-$C_{17}H_{35}$ SST-4™ is a polytetrafluoroethylene wax obtained from Shamrock Chemical Co. (melting point: 321°C)		

The recording materials prepared as described above were image-wise heated with a thermal head in a thermal printer so as to obtain a density of 3.2. The obtained minimum density in each case was less than 0.05. The obtained images were then visually inspected for scratches and artifacts in the image and assigned a number from 0 to 5 to indicate the amount of scratches and artifacts. A number of 0 indicates that no scratches or artifacts were found whereas a number of 5 indicates severe scratching or artifacts. The obtained results are listed in table 2.

Table 2

Sample no.	Artifacts	Scratches
1	4	5
2	2	4
3	2	2
4	1	4

From the above table it can be seen that the number of scratches and artifacts in the image can be reduced by adding a thermomeltable particle.

Claims

1. A recording material comprising on a support (i) a heat sensitive layer comprising a substantially light insensitive organic silver salt, (ii) a protective layer containing thermomeltable particles dispersed in a binder and (iii) a reducing agent being present in the heat sensitive layer and/or another layer on the same side of the support carrying the heat sensitive layer.

2. A recording material according to claim 1 wherein said binder is a polycarbonate.

3. A recording material according to claim 1 or 2 wherein said protective layer further comprises a lubricant or wherein a lubricant is present on top of said protective layer.

4. A recording material according to claim 1 wherein said binder is hydrophilic.

5. A recording material according to claim 4 wherein said binder is polyvinyl alcohol or a polyvinyl acetate.

6. A recording material according to any of the above claims wherein said protective layer is hardened.

7. A recording material according to claim 6 wherein a lubricant is hardened together with said binder of said protective layer.

8. A recording material according to any of the above claims wherein said thermomeltable particles are selected from amongst the group consisting of amide wax, Carnauba wax, polyethylene wax, and polytetrafluoroethylene wax.

9. A recording material according to any of the above claims wherein said protective layer further comprises a matting agent.

10. A method for making an image comprising image-wise heating a recording material as defined in any of the above claims by means of a thermal head contacting the protective layer of the recording material.

11. Image obtained by the method of claim 10 for use in medical diagnostics.

Patentansprüche

1. Ein Aufzeichnungsmaterial enthaltend auf einem Träger (i) eine wärmeempfindliche Schicht, die ein wesentlich lichtunempfindliches, organisches Silbersalz enthält, (ii) eine Schutzschicht, die in einem Bindemittel dispergierte, wärmeschmelzbare Partikeln enthält, und (iii) ein Reduktionsmittel, das sich in der wärmeempfindlichen Schicht und/oder in einer anderen Schicht auf der gleichen Trägerseite wie die wärmeempfindliche Schicht befindet.

2. Ein Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Bindemittel ein Poly(carbonat) ist.

3. Ein Aufzeichnungsmaterial nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Schutzschicht weiterhin ein Schiermittel enthält, oder daß sich ein Schmiermittel auf der Schutzschicht befindet.

4. Ein Aufzeichnungsmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Bindemittel hydrophil ist.

5. Ein Aufzeichnungsmaterial nach Anspruch 4, dadurch gekennzeichnet, daß das Bindemittel Poly(vinylalkohol) oder Poly(vinylacetat) ist.

6. Ein Aufzeichnungsmaterial nach irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Schutzschicht ausgehärtet ist.

7. Ein Aufzeichnungsmaterial nach Anspruch 6, dadurch gekennzeichnet, daß ein Schmiermittel zusammen mit dem Bindemittel der Schutzschicht ausgehärtet ist.

8. Ein Aufzeichnungsmaterial nach irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die wärmeschmelzbaren Partikeln aus der Gruppe bestehend aus Amidwachs, Carnaubawachs, Poly(ethylen)wachs und Poly(tetrafluorethylen)wachs gewählt werden.

9. Ein Aufzeichnungsmaterial nach irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Schutzschicht weiterhin ein Mattiermittel enthält.

10. Eine Methode zur Erzeugung eines Bildes, in der ein in irgendwelchem der vorstehenden Ansprüche definiertes Aufzeichnungsmaterial mittels eines Thermokopfes, der die Schutzschicht des Aufzeichnungsmaterials berührt, bildmäßig erhitzt wird.

11. Ein Bild, das man mittels der Methode von Anspruch 10 erzeugt hat, für den Gebrauch in der medizinischen Diagnostik.

Revendications

1. Un matériau enregistreur comprenant sur un support (i) une couche sensible à la chaleur comprenant un sel d'argent organique substantiellement insensible à la lumière, (ii) une couche de protection contenant des particules thermofusibles dispersées dans un liant et (iii) un agent réducteur se trouvant dans la couche sensible à la chaleur et/ou dans une autre couche se trouvant sur le même côté du support que la couche sensible à la chaleur.

2. Un matériau enregistreur selon la revendication 1, caractérisé en ce que le liant est un polycarbonate.

3. Un matériau enregistreur selon la revendication 1 ou 2, caractérisé en ce que la couche de protection comprend en plus un lubrifiant, ou caractérisé en ce qu'un lubrifiant est présent sur la couche de protection.

4. Un matériau enregistreur selon la revendication 1, caractérisé en ce que le liant est hydrophile.

5. Un matériau enregistreur selon la revendication 4, caractérisé en ce que le liant est un poly(alcool de vinyle) ou un poly(acétate de vinyle).

6. Un matériau enregistreur selon l'une quelconque des revendications précédentes, caractérisé en ce que la couche de protection est durcie.

7. Un matériau enregistreur selon la revendication 6, caractérisé en ce qu'un lubrifiant est durci ensemble avec le liant de la couche de protection.

8. Un matériau enregistreur selon l'une quelconque des revendications précédentes, caractérisé en ce que les particules thermofusibles sont choisies dans le groupe composé de cire d'amide, de cire de carnauba, de cire de polyéthylène et de cire de polytétrafluoroéthylène.

9. Un matériau enregistreut selon l'une quelconque des revendications précédentes, caractérisé en ce que la couche de protection comprend en plus un agent de matage.

10. Une méthode pour faire une image comprenant l'échauffement sous forme d'image d'un matériau enregistreur tel que défini dans l'une quelconque des revendications précédentes au moyen d'une tête thermique qui établit un contact avec la couche protectrice du matériau enregistreur.

11. Image obtenue par la méthode de la revendication 10 pour être utilisée dans le diagnostic médical.