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(54) Method for the formation of a heat mode image without pinhole defect

(57) A method is disclosed for the formation of a heat mode image strongly improved for pinhole defect. A thermal imaging medium contains, apart from its image forming layer and several auxiliary layers, also a reducible organic metal salt layer, preferably a silver behenate layer. After information-wise laser exposure, lamination of a stripping sheet and delamination a negative heat mode is obtained. By means of an overall post-exposure of this image the pinholes in full recorded areas disappear due to reduction of the metal salt.

In an alternative embodiment the metal salt layer is not present in the original thermal imaging medium but applied as part of a separate laminate on top of the processed negative heat mode image.

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Description

1. Field of the invention.

The present invention relates to a method for the formation of an improved heat mode image.

2. Background of the invention.

Conventional photographic materials based on silver halide are used for a large variety of applications. For instance, in the pre-press sector of graphic arts rather sensitive camera materials are used for obtaining screened images. Scan films are used for producing colour separations from multicolour originals. Phototype setting materials record the information fed to phototype- and image setters. Relative insensitive photographic materials serve as duplicating materials usually in a contact exposure process. Other fields include materials for medical recording, duplicating and hard copy, X-ray materials for non-destructive testing, black-and-white and colour materials for amateur- and professional still photography and materials for cinematographic recording and printing.

Silver halide materials have the advantage of high potential intrinsic sensitivity and excellent image quality. On the other hand they show the drawback of requiring several wet processing steps employing chemical ingredients which are suspect from an ecological point of view.

In the past several proposals have been made for obtaining an imaging element that can be developed using only dry development steps without the need of processing liquids as it is the case with silver halide photographic materials.

A dry imaging system known since quite a while is 3M's dry silver technology. It is a catalytic process which couples the light-capturing capability of silver halide to the image-forming capability of organic silver salts.

Another type of non-conventional materials as alternative for silver halide is based on photopolymerisation. The use of photopolymerizable compositions for the production of images by information-wise exposure thereof to actinic radiation is known since quite a while. All these methods are based on the principle of introducing a differentiation in properties between the exposed and non-exposed parts of the photopolymerizable composition e.g. a difference in solubility, adhesion, conductivity, refractive index, tackiness, permeability, diffusibility of incorporated substances e.g. dyes etc..

As a further alternative for silver halide chemistry dry imaging elements are known that can be image-wise exposed using an image-wise distribution of heat. When this heat pattern is applied directly by means of a thermal head such elements are called thermographic materials. When the heat pattern is applied by the transformation of intense laser light into heat these elements are called heat mode materials or thermal imaging media. They offer the advantage in addition to an ecological advantage that they do not need to be handled in a dark room nor is any other protection from ambient light needed. Heat mode recording materials, based on change of adhesion, are disclosed in e.g. US-P 4,123,309, US-P 4,123,578, US-P 4,157,412, US-P 4,547,456 and PCT publ. Nos. WO 88/04237, WO 93/03928, and WO 95/00342. In a preferred embodiment such a thermal imaging medium comprises a transparent support and an imaging layer containing carbon black, optionally additional layers and a stripping sheet. By the conversion of intense laser light into heat on information-wise exposure a surface part of the support liquefies and firmly locks the carbon black, so that after delamination a negative carbon black image is formed on the support.

When this kind of materials is exposed by specular laser radiation through a transparent support the following problem arises. Transparent polymeric resin supports such as polyethylene terephthalate supports tend to contain microscopic dust particles, or catalyst rest particles, or microscopic voids (so-called fish-eyes) which scatter the incoming laser beam so that it does not reach the radiation sensitive layer anymore at the proper location. In negative working systems this leads to the formation of so-called pinholes ; in positive working systems it causes the formation of so-called pinpoints. The same phenomenon is caused by the presence of dust or scratches on the surface of the support or in the optionally present subbing layer. In negative working heat mode systems, bases on change of adhesion as described above, the pinholes become apparent after the delamination step. The defect is most disturbing in recorded full areas, where the pinholes appear as tiny white spots on a black background, and less in recorded separate lines and dots. Although these pinholes, depending on their size are hardly disturbing for practical applications of the finished image, e.g. as a master for the exposure of a printing plate or of a duplicating material, they give the image an unsatisfactory outlook, especially when inspected by means of a magnifying glass.

It is the object of the present invention to provide an improved method for the formation of a heat mode image, based on change of adhesion, which is substantially free of pinholes.

Other objects of the invention will become clear from the description hereinafter.

3. Summary of the invention.

In a first general embodiment, the objects of the present invention are realized by providing a method for the formation of a heat mode image comprising the following steps :

(a) providing a thermal imaging medium comprising, in order :

(1) a transparent support,
(2) a subbing layer,
(3) a layer containing a reducible organic metal salt, a binder and a reducing agent,
(4) an image forming layer containing an image forming substance and a substance capable of transforming laser radiation into heat, being the same as or different from the image forming substance,
(5) a release layer, and
(6) a thermoadhesive layer,

in either order, (b) exposing information-wise said thermal imaging medium to laser radiation, and (c) laminating a stripping sheet (7) to said thermoadhesive layer (6), and
(d) delaminating, whereby in the exposed areas at least part of said release layer (5), said image forming layer (4), said layer (3), and said layer (2) adhere to said support (1) thus forming a negative heat mode image on said support, while in the unexposed areas the image forming layer (4), said layer (5) and said layer (6) are removed with said stripping sheet, and
(e) subjecting the obtained negative heat mode image to an overall exposure to active radiation.

In a second general embodiment, the objects of the present invention are realized by providing a method for the formation of a heat mode image comprising the following steps :

(a') providing a thermal element (A) comprising, in order :

(1') a transparent support,
(2') an image forming layer containing an image forming substance and a substance capable of transforming radiation into heat, being the same as or different from the image forming substance,
(3') a release layer, and
(4') a thermoadhesive layer,

in either order, (b') exposing information-wise said thermal element (A), and (c') laminating a stripping sheet (5') to said thermoadhesive layer (4'), and
(d') delaminating, whereby in the exposed areas at least part of said release layer (3'), and said image forming layer (2') adhere to said support (1') thus forming a negative heat mode image on said support, while in the unexposed parts said image forming layer (2'), said layer (3') and said layer (4') are removed with said stripping sheet (5'),
(e') providing a laminate (B) comprising, in order :

(6') a base,
(7') optionally a subbing layer, and
(8') a layer containing a reducible organic metal salt, a binder and a reducing agent,

(f') laminating laminate (B) to the negative heat mode image formed out of thermal element (A) by steps (a') to (d'), layer (8') of (B) and the at least part of layer (3') of (A) facing each other, and
(g') subjecting the obtained composite to an overall exposure to active radiation.

In both embodiments the pinhole defect is overcome by the density generated in layer (3) or (8').
Preferably the image forming substance is carbon black, and the organic reducible metal salt is silver behenate.

4. Detailed description of the invention.

First of all, the compositions of the different layers will be discussed in detail.
As transparent support for the thermal imaging medium for use in the present invention polyethylene terephthalate (PET) is preferred. However other transparent polymeric resins, e.g. polycarbonate, polyvinylchloride, polyethylene, polypropylene or polystyrene can be used.
In the first general embodiment of the present invention the transparent support, preferably PET, is provided with a subbing layer (2). An example of a suitable subbing layer is a layer containing a polymer containing covalently bound chlorine. Suitable chlorine containing polymers are e.g. polyvinyl chloride, polyvinylidene chloride, a copolymer of vinylidene chloride, an acrylic ester and itaconic acid, a copolymer of vinyl chloride and vinylidene chloride, a copolymer of vinyl chloride, vinylidene chloride and itaconic acid, a copolymer of vinyl chloride, vinyl acetate and vinyl alcohol, A preferred chlorine containing polymer is co(vinylidenechloride-methylacrylate-itaconic acid ; 88 % / 10 % : 2 %). A most

suitable subbing layer contains the latter polymer and a colloidal silica such as KIESELSOL 100F (Bayer AG).

Layer (3) or (8') (depending on the type of embodiment) contains as main ingredients a reducible metal salt, a reducing agent, a binder and optionally a toning agent. In a preferred embodiment the organic metal salt is an organic silver salt. Substantially light-insensitive organic silver salts particularly suited for use according to the present invention in the photosensitive recording layer 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. Silver salts of 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 can be used silver salts of aromatic carboxylic acids (e.g. benzoic acid, phtalic acid, terephtalic acid, salicylic acid, m-nitrobenzoic-, phenylacetic-, pyromellitic-, p-phenylbenzoic-, camphoric-, huroic-, acetamidobenzoic- and o-aminobenzoic acid, etc.). Furtheron can be used silver salts of mercapto group- or thione group-containing compounds (e.g., 3-mercapto-4-phenyl-1,2,4-triazole, 2-mercaptobenzimidazole, etc.) or an imino group-containing compound (e.g. benzotriazole or derivatives thereof as described in GB 1,173,426 and US 3,635,719, etc.). Further are mentioned silver imidazolates and the substantially light-insensitive inorganic or organic silver salt complexes described in US-P 4,260,677.

In a most preferred embodiment of the present invention the organic silver salt is silver behenate. The compound is colourless, stable toward visible light, insoluble in many volatile liquid vehicles, and moisture-resistant. It is produced in the desired physical form without difficulty and at reasonable cost.

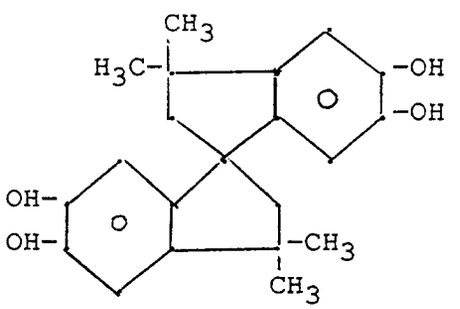
Other reducible organic metal salts beside silver salts include e.g. iron(III) stearate, iron(III) rosinate, iron(III) laurate, nickel stearate, nickel rosinate, nickel acetate, nickel oleate, copper rosinate, copper acetate, cobalt stearate, cobalt acetate and zinc stearate. A particular salt is often used in combination with a particular reducing agent in the donor element (see furtheron) in order to obtain optimal results.

The organic metal salt is preferably present in an amount between 1 and 20 mmole/m^2.

Suitable reducing agents for use in layer (3) or (8') include pyrogallol; 4-azeloyl-bis-pyrogallol; 4-stearyl pyrogallol; galloacetophenone; di-tertiary-butyl pyrogallol; gallic acid anilide; methyl gallate, ethyl gallate; normal- and iso-propyl gallate; butyl gallate; dodecyl gallate; gallic acid; ammonium gallate; ethyl protocatechuate; cetyl protocatechuate; 2,5-dihydroxy benzoic acid, 1-hydroxy-2-naphthoic acid; 2-hydroxy, 3-naphthoic acid; phloroglucinol; catechol; 2,3-naphthalene diol; 4-lauroyl catechol; sodium gallate; protocatechualdehyde; 4-methyl esculetin; 3,4-dihydroxy benzoic acid; 2,3-dihydroxy benzoic acid; the esters of the mentioned acids; hydroquinone; 4,4'-dihydroxy biphenyl; 3,4-dihydroxyphenylacetic acid; 4(3',4'-dihydroxyphenylazo)benzoic acid; 2,2'-methylene bis-3,4,5-trihydroxybenzoic acid; ortho- and para-phenylene diamine; tetramethyl benzidine; 4,4',4''-diethylamino triphenylmethane; o-, m-, and p-aminobenzoic acid; alpha and beta naphthols; 4-methoxy, 1-hydroxy-dihydronaphthalene; and tetrahydroquinoline.

Other useful reducing agents include resorcins, m-aminophenols, alkylphenols, alkoxynaphtols, m-phenylenediamines. A further class of reducing agents is constituted by hydrazine compounds. Especially preferred hydrazine compounds include p-tolylhydrazine hydrochloride, N,N-phenylformylhydrazide, acetohydrazide, benzoylhydrazide, p-toluenesulphonylhydrazide, N,N'-diacetylhydrazine, β-acetyl-phenylhydrazine, etc.

Another possible reducing agent is "Spirana", disclosed in European patent application Appl. No. 92203495, and corresponding to following chemical formula :



The reducing agents may be used in combination if desired.

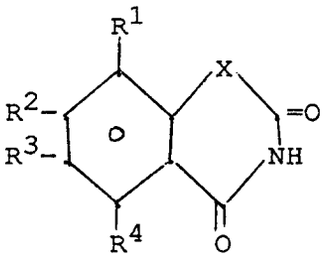
Particular organic metal salts of the photosensitive element, especially when they are not organic silver salts, are often preferably used with particular reducing agents in order to optimize the reduction reaction. Examples of such preferred "reaction pairs" can be found e.g. in US 3,722,406, col. 3, table 1.

When the reducible metal salt is silver behenate the reducing agent is preferably chosen from ethyl gallate or the butyl ester of 3,4-dihydroxy benzoic acid.

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 the organic metal salt and/or the reducing agent a so-called toning agent known from thermography or photo-thermography. Preferably this toning agent is incorporated in the photosensitive element but in principle it can also be present in the donor element.

Suitable toning agents are the phthalimides and phthalazinones mentioned in US-P 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 :



wherein

X represents O or NR^5;

each of R^1, R^2, R3 and R^4 (same or different) represents hydrogen, alkyl, e.g. C_1-C_{20} alkyl, preferably C_1-C_4 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 R^1 and R^2 or R^2 and R^3 represent the ring members required to complete a fused aromatic ring, preferably a benzene ring, or R^3 and R^4 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 preferred toner compound is 3,4-dihydro-2,4-dioxo-1,3,2H-benzoxazine described in US-P 3,951,660.

Examples of useful binders for the organic metal salt layer include organic solvent-soluble polymers, e.g. polymers derived from α,β-ethylenically unsaturated compounds such as e.g. polymethyl methacrylate, polyvinyl chloride, a vinylidene chloride-vinyl chloride copolymer, polyvinyl acetate, a vinyl acetate-vinyl chloride copolymer, a vinylidene chloride-acrylonitrile copolymer, a styrene-acrylonitrile copolymer. chlorinated polyethylene, chlorinated polypropylene, a polyester, a polyamide, etc. An especially preferred halogen-free binder, which is ecologically interesting, is polyvinylbutyral containing some vinyl alcohol units (sold under the trade name BUTVAR by MONSANTO Co). Several organic solvents can be used for dissolving and coating these polymers. These polymer binders may be used either alone or in combination of two or more thereof. Also they can be combined with water-soluble binders, e.g. gelatin, polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, methyl cellulose, ethyl cellulose, gum arabic, casein, etc. 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.

In the image forming layer (4) or (2') (depending on the embodiment type) the image forming substance is preferably a pigment, e.g. a magnetic pigment, e.g. iron oxides, a coloured piment, e.g. copper phtalocyanine, or metal particles. However the most preferred pigment is carbon black. It can be used in the amorphous or in the graphite form. The preferred average particle size of the carbon black ranges from 0.01 to 1 μm. Different commercial types of carbon black can be used, preferably with a very fine average particle size, e.g. RAVEN 5000 ULTRA II (Columbian Carbon Co.), CORAX L6, FARBRUSS FW 2000, SPEZIALSCHWARZ 5, SPEZIALSCWARZ 4A, SPEZIALSCHWARZ 250 and PRINTEX U (all from Degussa Co.).

When using carbon the image forming substance and the compound transforming intense laser radiation into heat is one and the same product. When however the image forming substance is another compound not absorptive for the laser radiation, which is preferably infra-red laser radiation, an extra compound, preferably an infrared absorbing compound is required for transforming the radiation into heat. This infra-red absorbing compound can be a soluble infra-red absorbing dye or a dispersable infra-red absorbing pigment. Infra-red absorbing compounds are known since a long time and can belong to several different chemical classes, e.g. indoaniline dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds and squarylium derivatives.

A suitable infra-red dye can be chosen from the numerous disclosures and patent applications in the field, e.g., from US-Patent No's 4,886,733, 5,075,205, 5,077,186, 5,153,112 5,244,771, from Japanese unexamined patent publications (Kokai) No.'s 01-253734, 01-253735, 01-253736, 01-293343, 01-234844, 02-3037, 02-4244, 02-127638, 01-

227148, 02-165133, 02-110451, 02-234157, 02-223944, 02-108040, 02-259753, 02-187751, 02-68544, 02-167538, 02-201351, 02-201352, 03-23441, 03-10240, 03-10239, 03-13937, 03-96942, 03-217837, 03-135553, 03-235940, and from the European published patent applications publ. No.'s 0 483 740, 0 502 508, 0 523 465, 0 539 786, 0 539 978 and 0 568 022, and from European patent application appl. No. 94200797. This list is far from exhaustive and limited to rather recent disclosures.

It will be clear that mixtures of pigments, or mixtures of one or more pigments and one or more compounds transforming radiation into heat can be used.

As binders for the image forming layer gelatin, polyvinylpyrrolidone, polyvinylalcohol, hydroxyethylcellulose, polyethyleneoxide and a broad variety of polymer latices can be considered. These latices can be film forming or non-film forming. They can comprise acid groups as a result of which they can swell in an alkaline coating medium and/or become totally or partially soluble. In this way the layer properties can be strongly influenced, e.g. less coating and drying point defects will appear. When choosing a particular type of carbon black and a particular type of polymeric binder the ratio of the amounts of both has to be optimized for each case. Preferred binders are copolymers of ethylacrylate, methylacrylate and methacrylic acid.

The thickness of the image forming layer is preferably comprised between 0.5 and 1.5 micron.

The release layer contains a binder and one or more of the typical ingredients for release layers known in the art such as waxes, polyethylene, silicones, fluorated polymers such as Teflon, silica particles (e.g. SEAHOSTAR KE types, Nippon Shokukai Co), colloidal silica, polymeric beads (e.g. polystyrene, polymethylmethacrylate), hollow polymeric core/sheat beads (e.g. ROPAQUE particles, Rohm and Haas Co), beads of siliconised pigments like siliconised silica (e.g. TOSPEARL types, Toshiba Silicones Co), and matting agents. In a particularly preferred embodiment of the present invention the release layer contains a mixture of polyethylene and a per(fluoroethylene) compound (Teflon). The preferred coverage of the release layer ranges between 0.1 and 3 g/m^2.

The thermal adhesive layer (6) or (4') (or "thermoadhesive layer", or "TAL") contains one or more thermoadhesive polymers having a glass transition temperature T_g preferably comprised between 20 and 60 °C. For ecological and practical reasons the TAL is preferably coated from an aqueous medium. Therefore the polymers are preferably incorporated as latices. Other additives can be present into the TAL to improve the layer formation or the layer properties, e.g. thickening agents, surfactants, levelling agents, thermal solvents and pigments.

Preferred latices are styrene-butadiene latices. These latices can contain other comonomers which improve the stablitity of the latex, such as acrylic acid, methacrylic acid and acrylamide. Other possible polymer latices include polyvinylacetate, copoly(ethylene-vinylacetate), copoly(acrylonitrile-butadiene-acrylic acid), copoly(styrene-butylacrylate), copoly(methylmethacrylate-butadiene), copoly(methylmethacrylate-butylmethacrylate), copoly(methylmethacrylate-ethylacrylate), copolyester(terephtalic acid-sulphoisophtalic acid-ethyleneglycol), copolyester(terephtalic acid-sulphoisophtalic acid-hexanediol-ethyleneglycol).

Particularly suitable polymers for use in the TAL layer are the BAYSTAL polymer types, marketed by Bayer AG, which are on the basis of styrene-butadiene copolymers. Different types with different physical properties are available. The styrene content varies between 40 and 80 weight %, while the amount of butadiene varies between 60 and 20 weight % ; optionally a few weight % (up to about 10 %) of acrylamide and/or acrylic acid can be present. Most suited are e.g. BAYSTAL KA 8558, BAYSTAL KA 8522, BAYSTAL S30R and BAYSTAL P1800 because they are not sticky at room temperature when used in a TAL layer. Other useful polymers are the EUDERM polymers, also from Bayer AG, which are copolymers comprising n.-butylacrylate, methylmethacrylate, acrylonitrile and small amounts of methacrylic acid.

Alternatively to direct coating on top of the release layer the TAL can be coated on a separate temporary support. In that case the TAL is laminated to the release layer and then the temporary support is removed by delamination.

In principle there can be more than one TAL or the release layer also can contain a thermoadhesive polymer.

The stripping sheet can be laminated to the thermoadhesive layer after or before laser exposure. In the case where the lamination of the stripping sheet is performed before exposure the stripping sheet self-evidently must be transparent to the laser radiation. This transparent stripping sheet can be composed of any of the same polymeric resins suitable for use as support. As for the support (1) a polyethylene terephthalate sheet is preferred. Its thickness if preferably comprised between 10 and 200 μm. Preferably it is somewhat thinner than the support for ecological reasons. When the medium is exposed before lamination the stripping sheet can also be an opaque sheet such as a paper base, e.g. a plain paper base or a polyethylene coated paper.

After discussing the main ingredients of the different layers the possible layer arrangements and processes for successfully practicing the present invention will now be explained.

In a first general embodiment, the reducible metal salt layer is incorporated directly into the medium. The original layer arrangement and the status after processing are illustrated in fig. 1(I) and fig. 1(II), respectively. Following layer arrangement is provided, in order : support (1), subbing layer (2), reducible metal salt layer (3), image forming layer (4), release layer (5) and thermoadhesive layer (6). After information-wise laser exposure, lamination of a stripping sheet (7) and delamination (see furtheron) a negative heat mode image is obtained comprising at least part of layer (5) and the layers (4), (3) and (2) which all adhere to the original support (1). After delamination layer (4) shows a lot of pinholes

(see vertical white bars in fig. 1(II)). An overall exposure to active radiation is applied to the negative image. By active radiation is meant radiation that according to its nature and intensity is capable of generating sufficient beat in the recorded full areas. This overall exposure can be a lamp exposure, preferably an infra-red lamp exposure, but, most preferably, it is simply a scanning-wise exposure by the same laser as used for the information-wise exposure. Due to lateral spread of the heat generated and to its partial diffusion in layer (3) chemical reduction is induced in this layer (3). The density obtained, though be it a small one, is sufficient to fill up the white pinhole spots so that they are no longer visible. On a recorded isolated line or dot the generation and diffusion of heat is too insignificant to cause a broadening of that line or dot.

In a particular variation according to this first general embodiment a thin polymeric film forming layer (3bis) is incorporated between layer (3) and layer (4). In this case layer (4) is locked to layer (3bis) in the exposed parts. Self-evidently this layer is also present in the layer pack forming the negative heat mode image after exposure and further treatment. This extra layer must show a good adhesion to the reducible metal layer (3). This layer must be thin, otherwise the diffusion of heat to layer (3) coming from layer (4) will be insufficient. The thickness of this layer is preferably comprised between 0.1 and 1 μm. With this particular embodiment the residual pinhole level is even lower than without this extra layer and practically reduced to zero. Preferably this thin polymeric film forming layer is composed of polyethylene terephthalate coated from an organic solvent. This particular embodiment is illustrated by fig. 2.

In a second general embodiment of the present invention the metal salt layer is not incorporated in the original medium but is applied later after image formation and processing by means of a separate laminate. So on the one hand a thermal element (A) is provided comprising, in order, a support (1'), an image forming layer (2'), a release layer (3') and a thermoadhesive layer (4'). After exposure, lamination of a stripping sheet (5') and delamination, a negative heat mode image is obtained composed of at least part of layer (3') and layer (2') both adhering to support (1'). Again, after delamination, layer (2') shows a lot of pinholes. On the other hand a laminate (B) is provided comprising a base (6'), preferably also a PET base, optionally a subbing layer (7') and a reducible metal salt layer (8'). Then this laminate is laminated to the negative image formed out of thermal element (A). By a similar overall exposure as explained above the pinhole defect is overcome by a similar mechanism as explained for the first general embodiment. The second embodiment is illustrated by fig. 3(I) (original thermal element A), 3(II) (element A after lamination and delamination), and 3(III) (lamination of laminate B to the negative image $(A)_n$ derived from A).

The information-wise and/or overall scanning laser exposure can be performed by an Ar ion laser, a HeNe laser, a Kr laser, a frequency doubled Nd-YAG laser, a dye laser emitting in the visual spectral region. However in the preferred embodiment where the radiation to heat converting compound is an infra-red absorbing compound the laser is an infra-red laser. Especially preferred lasers are semiconductor diode lasers or solid state lasers such as a Nd-YAG laser emitting at 1064 nm, or a Nd-YLF laser emitting at 1053 nm.. Other possible infra-red laser types include diode lasers emitting at 823 nm or diode lasers emitting at 985 nm. Important parameters of the laser recording are the spot diameter (D) measured at the $1/e^2$ value of the intensity, the applied laser power on the film (P), the recording speed of the laser beam (v) and the number of dots per inch (dpi).

In the case of an overall lamp exposure preferably an infra-red lamp is used.

As stated above the lamination of the stripping sheet to the TAL can be performed before or after the laser exposure. Lamination may be conducted by putting the two materials in contact and then introducing the materials into the nip of a pair of heated laminating rollers under suitable pressure. Suitable laminating temperatures usually range from approximately 60°C to 100°C, preferably from 70°C to 90°C. The lamination temperature may not be too high in order to avoid total blackening of the organic metal salt layer.

The delamination can be performed manually or in a delamination apparatus. In a preferred way of doing the stripping layer is held planar and the medium is peeled off at an angle of about 180° at a speed of about 10 m/min.

When the information recorded as heat mode image, improved for pinhole defect, is provided by a phototype- or image-setter the heat mode image can be used as a master for the exposure of a printing plate or a graphic arts duplicating material.

The present invention will now be illustrated by the following examples without however being limited thereto.

EXAMPLES

EXAMPLE 1

A thermal imaging medium is prepared by coating on a polyethylene terephthalate support (1) having a thickness of 100 μm, the following layers, in order, :

(2) a subbing layer containing colloidal silica and copoly(vinylidenechloride-methylacrylate-itaconic acid ; 88 % / 10 % / 2 %) ;

(3) a layer containing silver behenate, BUTVAR B79 (Monsanto) as binder, silicone oil BAYSILON OIL A (Bayer AG), the butylester of 3,4-dihydroxybenzoic acid as reducing agent, and 3,4-dihydroxy-2,4-dioxo-1,3,2H-benzox-

azine as toning agent ;

(4) a carbon layer (C-layer) containing CORAX L6 carbon black, copoly(ethylacrylate-methylmethacrylate-methacrylic acid) ; 60 % / 23 % / 17 %) as binder and ULTRAVON W (Ciba-Geigy) as wetting agent.

(5) a release layer (RL) containing a polyethylene dispersion, Teflon (Hostaflon TF VP23D, Hoechst AG), BAYSTAL KA8522 (Bayer AG) and gelatin ;

(6) a thermoadhesive layer (TAL) containing BAYSTAL KA8522.

The composition of the different layers is represented in table 1.

TABLE 1

layer	composition	amount (g/m^2)
TAL (6)	BAYSTAL KA8522	25
RL (5)	polyethylene,	0.5
"	Teflon	0.25
"	BAYSTAL KA8522	0.75
"	gelatin	0.1
C-layer (4)	CORAX L6	1.0
"	co(EA-MMA-MAA)	0.8
"	ULTRAVON	0.4
layer (3)	BUTVAR B79	3.8
"	silver behenate	3.8
"	BAYSILON OIL A	0.014
"	reducing agent	0.9
"	toning agent	0.275
layer (2)	silica + co($ViCl_2$-MA-IA)	0.2

The thus prepared thermal imaging medium was information-wise exposed to intense laser radiation according to the following specifications :

- laser type : NdYLF emitting at 1053 nm ;
- laser spot diameter : 18 μm ($1/e^2$) ;
- linear recording speed : 32 m/s ;
- laser power on film : 1 W.

Full areas and a dot and line pattern were recorded.

A 100 μm thick polyethylene terephthalate stripping sheet was laminated on top of the exposed thermal imaging medium at 85 °C at a speed of 0.5 m/min. Then this stripping sheet was kept flat and the film was delaminated at an angle of 180° with a speed of 10 m/min approximately. In the exposed areas, part or release layer (5), the carbon layer (4), and the layers (3) and (2) adhered to support (1) giving rise to a negative heat mode image on that original support, while the unexposed areas the carbon layer, the release layer, and the thermoadhesive layer were removed with the PET stripping sheet.

In the full areas of the recorded image many pinholes were clearly visible. The finished negative image was then exposed to an overall scanning-wise laser exposure. By the transformation of radiation into heat in the carbon layer (4) and thanks to lateral spread and diffusion of the produced heat reduction of silver behenate to metallic silver was induced in the adjacent layer (3) even in the pinhole areas. As a result density was built up in this layer (3) causing the disappearance of the pinholes (less than 1 pinhole per cm^2). The Dmax values of the final negative heat mode image were 3.0 (visual filter) and 3.5 (UV filter). The Dmin values were 0.05 (vis.) and 0.07 (UV).

EXAMPLE 2

The thermal imaging medium of this example was similar to the one of the previous example with the exception that a polyethylene terephtalate film forming layer (3bis) was coated from the organic solvent hexafluoroisopropanol between layer (3) and layer (4). So the composition of the thermal imaging medium was as represented by table 2 :

TABLE 2

layer	composition	amount (g/m^2)
TAL (6)	BAYSTAL KA8522	25
RL (5)	polyethylene	0.5
"	Teflon	0.25
"	BAYSTAL KA8522	0.75
"	gelatin	0.1
C-layer (4)	CORAX L6	1.0
"	co(EA-MMA-MAA)	0.8
"	ULTRAVON	0.4
layer (3bis)	coated PET	0.2
layer (3)	BUTVAR B79	3.8
"	silver behenate	3.8
"	BAYSILON OIL A	0.014
"	reducing agent	0.9
"	toning agent	0.275
layer (2)	silica + co($ViCl_2$-MA-IA)	0.2

The exposure and further treatment was identical to example 1. An image with a still better resolution and without pinholes was eventually obtained.

EXAMPLE 3

A thermal element (A) was prepared comprising, in order, an unsubbed polyethylene terephthalate support (1'), a carbon containing image forming layer (2'), a release layer (3') and a TAL (4'). The composition is illustrated in table 3.

TABLE 3

layer	composition	amount (g/m^2)
TAL (4')	BAYSTAL KA8522	25
RL (3')	polyethylene	0.5
"	Teflon	0.25
"	BAYSTAL KA8522	0.75
"	gelatin	0.1
C-layer (2')	CORAX L6	1.0
"	co(EA-MMA-MAA)	0.8
"	ULTRAVON	0.4

On the other hand a laminate (B) was prepared comprising, in order, a polyethylene terephthalate support (6'), a subbing layer (7') and a silver behenate + reducing agent containing layer (8'). The composition is represented in table 4.

TABLE 4

layer	composition	amount (g/m^2)
layer (8')	BUTVAR B79	3.8
"	silver behenate	3.8
"	BAYSILON OIL A	0.014
"	reducing agent	0.9
"	toning agent	0.275
layer (7')	silica + co($ViCl_2$-MA-IA)	0.2

The reducing agent and the toning agent were the same as in the previous examples.

The thermal element (A) was subjected to the same exposure, lamination (by means of a PET stripping sheet (5')) and delamination steps as the thermal imaging medium of the previous examples. In the exposed areas, part of release layer (3') and carbon layer (2') adhered to PET support (1'), while in the unexposed areas the carbon layer (2'), the release layer (3') and the TAL (4') were removed with the PET stripping sheet (5'). A negative heat mode image showing a lot of pinholes in the recorded full areas was obtained on the original support (1') of thermal element (A).

Then laminate (B) was laminated to the negative heat mode element formed out of thermal element (A), layer (8') of (B) and the left over part of layer (3') facing each other, at 85 °C and at a speed of 0.5 m/min.

Finally, this composite was subjected to an overall scanning-wise laser exposure. By the mechanism of generation of heat, diffusion and lateral spread of that heat, and reduction of silver behenate, a final heat mode image was obtained without pinholes.

Claims

1. Method for the formation of a heat mode image comprising the following steps :

   (a) providing a thermal imaging medium comprising, in order :

   (1) a transparent support,
   (2) a subbing layer,
   (3) a layer containing a reducible organic metal salt, a binder and a reducing agent,
   (4) an image forming layer containing an image forming substance and a substance capable of transforming laser radiation into heat, being the same as or different from the image forming substance,
   (5) a release layer, and
   (6) a thermoadhesive layer,

   in either order, (b) exposing information-wise said thermal imaging medium to laser radiation, and (c) laminating a stripping sheet (7) to said thermoadhesive layer (6), and
   (d) delaminating, whereby in the exposed areas at least part of said release layer (5), said image forming layer (4), said layer (3), and said layer (2) adhere to said support (1) thus forming a negative heat mode image on said support, while in the unexposed areas the image forming layer (4), said layer (5) and said layer (6) are removed with said stripping sheet, and
   (e) subjecting the obtained negative heat mode image to an overall exposure to active radiation.

2. Method according to claim 1 wherein said reducible organic metal salt is a reducible organic silver salt.

3. Method according to claim 2 wherein said reducible organic silver salt is silver behenate.

4. Method according to any of claims 1 to 3 wherein said image forming substance is a pigment.

5. Method according to claim 4 wherein said pigment is carbon black, being at the same time the substance capable of transforming laser radiation into heat.

6. Method according to any of claims 1 to 5 wherein said layer (3) further contains a toning agent.

7. Method according to any of claims 1 to 6 wherein said release layer contains a mixture of polyethylene and a per(fluoroethylene) compound.

8. Method according to any of claims 1 to 7 wherein said information-wise exposure to laser radiation is performed by a laserdiode or a semiconductor laser.

9. Method according to any of claims 1 to 8 wherein said overall exposure to radiation is an overall scanning-wise exposure to the same laser radiation as used for the information-wise exposure.

10. Method according to any of claims 1 to 9 wherein said thermal imaging medium further comprises a polymeric film forming layer (3bis), positioned between said layer (3) and said layer (4), having a dry thickness comprised between 0.1 and 1 μm, and being adhesive to said layer (3).

11. Method according to claim 10 wherein said polymeric film forming layer is a polyethylene terephthalate layer coated from an organic solvent.

12. Method for the formation of a heat mode image comprising the following steps :

(a') providing a thermal element (A) comprising, in order :

(1') a transparent support,
(2') an image forming layer containing an image forming substance and a substance capable of transforming radiation into heat, being the same as or different from the image forming substance,
(3') a release layer, and
(4') a thermoadhesive layer,

in either order, (b') exposing information-wise sad thermal element (A), and (c') laminating a stripping sheet (5') to said thermoadhesive layer (4'), and
(d') delaminating, whereby in the exposed areas at least part of said release layer (3'), and said image forming layer (2') adhere to said support (1') thus forming a negative heat mode image on said support, while in the unexposed parts said image forming layer (2'), said layer (3') and said layer (4') are removed with said stripping sheet, and
(e') providing a laminate (B) comprising, in order :

(6') a base,
(7') optionally a subbing layer, and
(8') a layer containing a reducible organic metal salt, a binder and a reducing agent,

(f') laminating laminate (B) to the negative heat mode image formed out of thermal element (A) by steps (a') to (d'), layer (8') of (B) and the at least part of layer (3') of (A) facing each other, and
(g') subjecting the obtained composite to an overall exposure to active radiation.

13. Method according to claim 12 wherein said reducible organic metal salt is a reducible organic silver salt.

14. Method according to claim 13 wherein said reducible organic silver salt is silver behenate.

15. Method according to any of claims 12 to 14 wherein said image forming substance is a pigment.

16. Method according to claim 15 wherein said pigment is carbon black, being at the same time the substance capable of transforming laser radiation into heat.

17. Method according to any of claims 12 to 16 wherein said layer (8') further contains a toning agent.

18. Method according to any of claims 12 to 17 wherein said release layer (3') contains a mixture of polyethylene and

a per(fluoroethylene) compound.

19. Method according to any of claims 12 to 18 wherein said information-wise exposure to laser radiation is performed by a laserdiode or a semiconductor laser.

20. Method according to any of claims 12 to 19 wherein said overall exposure to radiation is an overall scanning-wise exposure to the same laser radiation as used for the information-wise exposure.

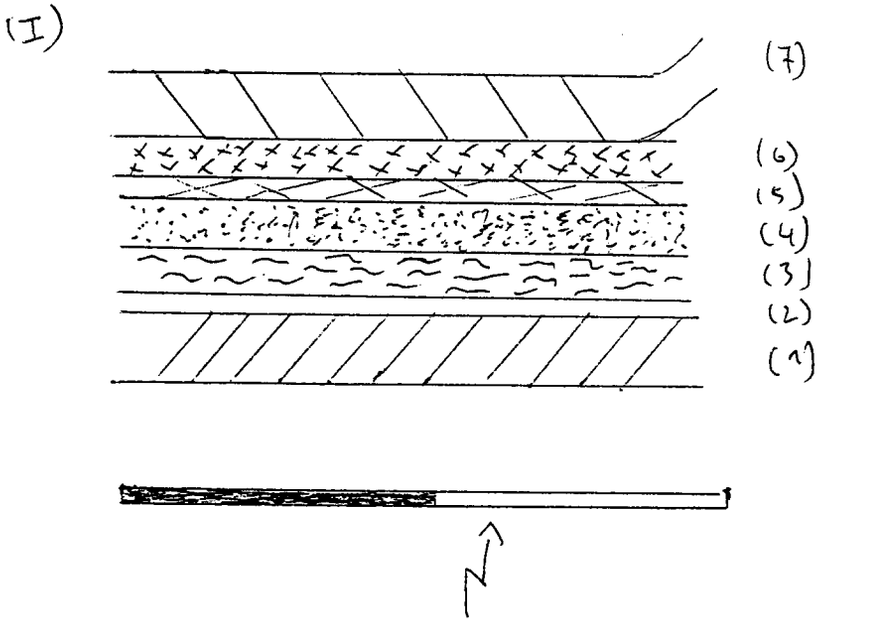


fig. 1

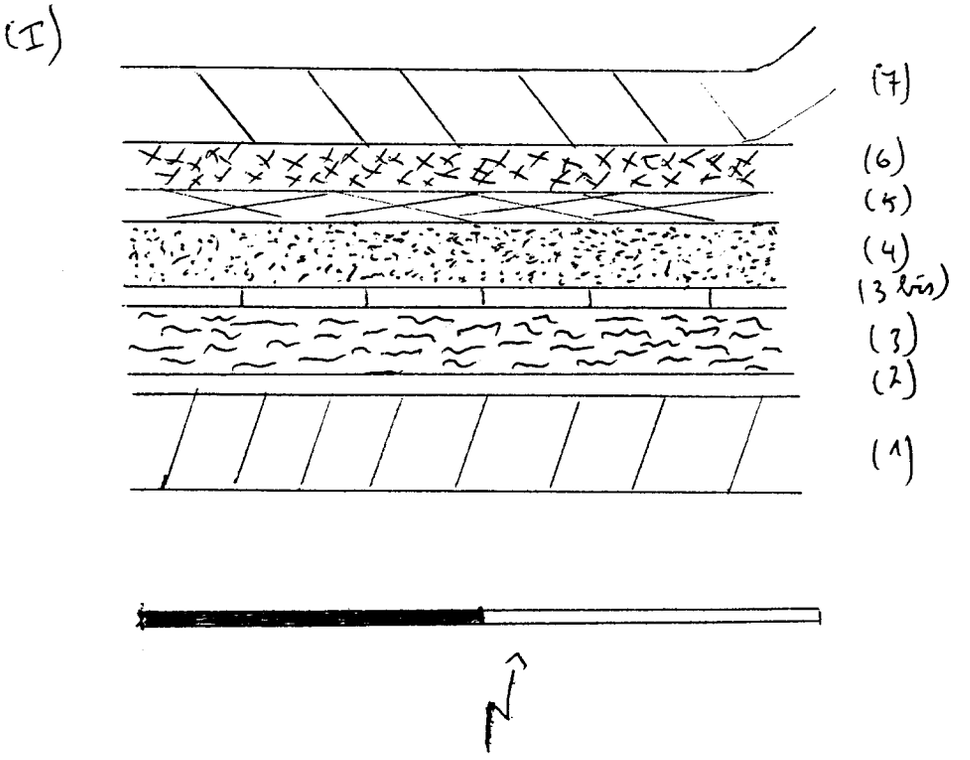


fig 2

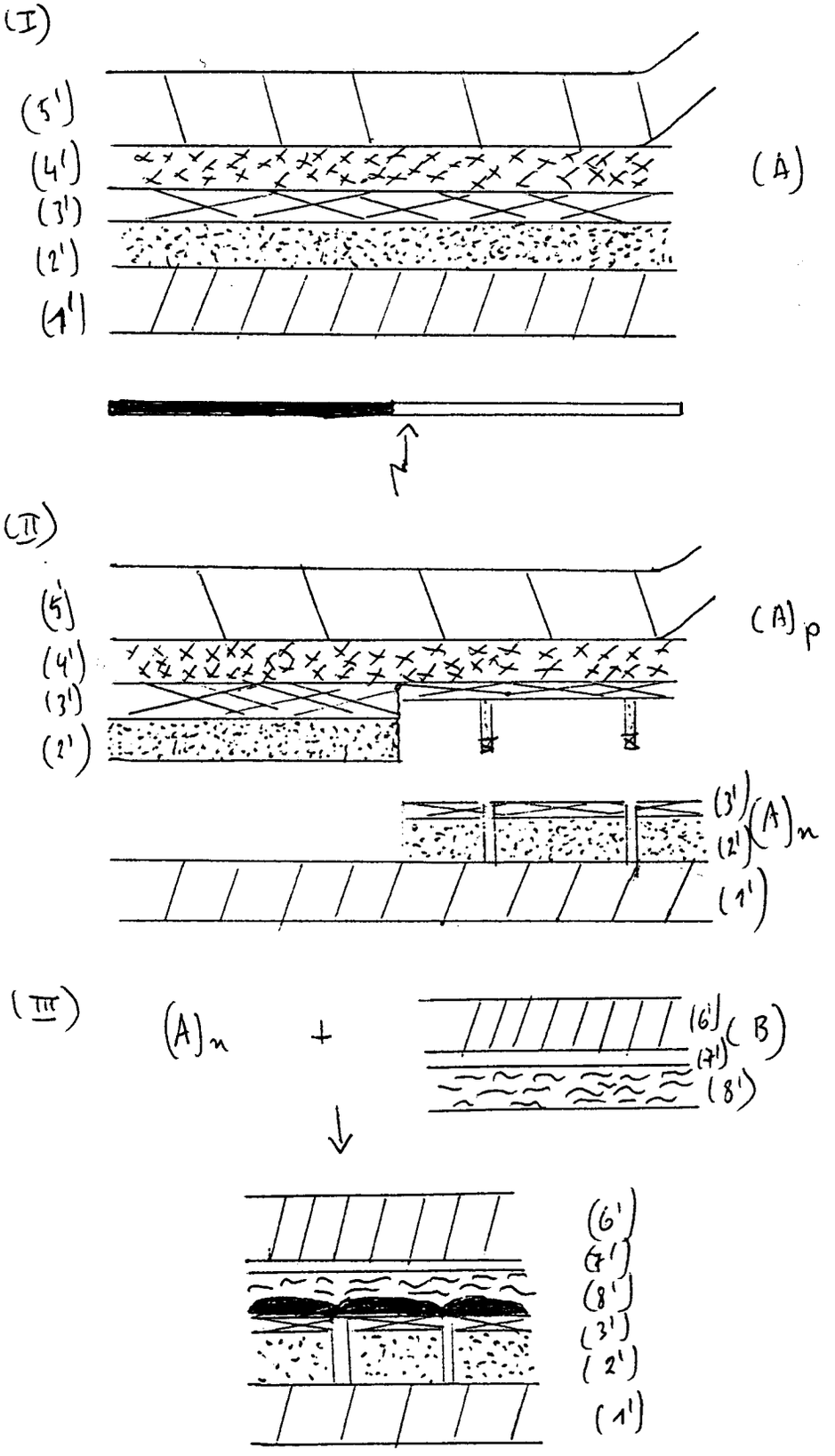


fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 3208

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP-A-0 599 368 (AGFA GEVAERT NV) 1 June 1994 * the whole document * ---	1-20	B41M5/40 B41M5/38 G03C1/498
Y	WO-A-95 00342 (AGFA GEVAERT NV ;UYTTERHOEVEN HERMAN JOZEF (BE); BASTIAENS LUC GUS) 5 January 1995 * the whole document * ---	1-20	
Y	RESEARCH DISCLOSURE, no. 374, 1 June 1995, pages 378-383, XP000519431 "IMPROVED THERMAL IMAGING MEDIUM" * the whole document * -----	1-20	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C
B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 July 1996	Rasschaert, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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