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(54) Method for the formation of a heat mode image

(57) A thermal imaging medium comprises a support, an image forming layer preferably containing carbon black, and an adhesive top layer with a strong adhesion towards that image forming layer. On exposure by intense laser radiation the image forming layer is image-wise released from the adhesive layer. By means of a lamination/delamination procdure with a stripping sheet the unexposed parts are removed while the exposed parts remain adhered to the original support. A final heat mode image is obtained with reduced level of physical defects and with low Dmin.

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Description

1. Field of the invention.

The present invention relates to the formation of a 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. In order to obtain a sufficient development of heat the laser exposure must be performed through the transparent support so that the heat can be generated on the interface support/carbon layer.

Still other heat mode image forming systems are based on ablation. Mostly in these systems the recorded image is transferred to an acceptor sheet. As a consequence such an acceptor must be applied by lamination before the recording step, as disclosed e.g. in US 4,245,003. In still another technique the image forming parts are image-wise released from a top carrier, as disclosed e.g. in unexamined Japanes patent publication JP-A 56-117965. For both systems a second foil must be applied before recording. This has as a consequence that the final image quality can be gravely deteriorated by physical defects, such as the occurence of pinholes, resulting from lamination faults or contact problems between acceptor and donor during recording. Furtheron most systems based on ablation suffer from too high a minimum density in the final image.

The present invention extends the teaching of image formation based on heat mode.

It is the object of the present invention to provide a method for the formation of an image based on heat mode with a reduced level of physical defects.

It is a further object of the present invention to provide a method for the formation of an image based on heat mode with a sufficiently low minimum density.

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

3. Summary of the invention.

The objects of the present invention are realized by providing a method for the formation of a heat mode image comprising the following steps :

(1) providing a thermal imaging medium comprising :

(a) a support,
(b) an image forming layer containing a binder, an image forming substance and a radiation to heat converting substance, which can be the same as or different from the image forming substance,
(c) an adhesive or thermoadhesive layer transparent for laser radiation, wherein the adhesive force between said (thermo)adhesive layer and said image forming layer is larger than the adhesive force between said image forming layer and said support.

(2) exposing information-wise by laser radiation through the side coated with (b) and (c) said thermal imaging medium whereby the adhesive force between said (thermo)adhesive layer and said image forming layer is lowered to a value smaller than that of the adhesive force between said image forming layer and said support,
(3) laminating a stripping sheet on top of said thermal imaging medium, and delaminating, whereby the unexposed areas are removed with the (thermo)adhesive layer and the stripping sheet thus forming a positive image on said stripping sheet, while the exposed areas remain adhered to said support thus forming a negative image on said support.

In a perferred embodiment the image forming substance is carbon black being at the same time the radiation to heat converting substance.

4. Detailed description of the invention.

The basic idea of the present invention is as follows. If it is not necessary to apply a laminate before laser exposure the above cited problems in connection with physical defects will not occur. Instead of applying a laminate a top layer is coated which has a very strong adhesion to the laser absorbing image forming layer. By intense laser exposure through the coated side (contrary to the embodiments of e.g. WO 88/04237 and WO 95/00342) the adhesion of this top layer to the image forming layer is lowered to a level below the adhesion of the image forming layer to the support. In this way an image-wise release in the exposed areas of the image forming layer from the top adhesive layer occurs. In this way no transfer of the image density occurs but the image forming layer remains adhered to the original support in the exposed areas. After information-wise exposure of the thermal imaging medium a stripping sheet (or so-called "cleaning foil") is applied on top by cold or warm lamination. On subsequent delamination the non-exposed parts of the image forming layer are removed together with the adhesive layer and the cleaning foil. In this way a sufficiently low Dmin is obtained.

The compositions of the different layers will now 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. It will be readily understood the the polymeric support is preferably unsubbed ; otherwise the easy removal of the unexposed parts would seriouly be hampered.

In principle also an opaque support such as polyethylene- or polypropylene coated paper can be used, but most preferably the support is transparent. In this way the finished image can serve as intermediate for a further copying step or for exposure of a printing plate.

In the image forming layer (b) 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 infra-red 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 infrared 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 (b) gelatin, polyvinylpyrrolidone, polyvinylalcohol, nitrocellulose, 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. Another preferred binder is nitrocellulose.

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

The adhesive layer (c) can contain a permanent adhesive, also called pressure-sensitive adhesive polymer, or a thermoadhesive, also called heat-sensitive polymer. A survey of pressure and/or thermal adhesives is given by J. Shields in "Adhesives Handbook", 3rd. ed. (1984), Butterworths - London, Boston, and by Ernest W. Flick in "Handbook of Adhesive Raw Materials" (1982), Noyens Publications, Park Ridge, New Jersey - USA.

Examples of pressure-sensitive adhesive resins are described in US-P 4,033,770 for use in the production of adhesive transfers (decalcomanias) by the silver complex diffusion transfer process, in the Canadian Patent 728,607 and in the United States Patent 3,131,106. Pressure-sensitive adhesives are usually composed of (a) thermoplastic polymer(s) having some elasticity and tackiness at room temperature (about 20°C), which is controlled optionally with a plasticizer and/or tackifying resin. A thermoplastic polymer is completely plastic if there is no recovery on removal of stress and completely elastic if recovery is instantaneous and complete.

Particularly suitable pressure-sensitive adhesives are selected from the group of polyterpene resins, low density polyethylene, a copoly(ethylene/vinyl acetate), a poly(C_1-C_{16})alkyl acrylate, a mixture of poly(C_1-C_{16})alkyl acrylate with polyvinyl acetate, and copoly(vinylacetate-acrylate) being tacky at 20°C.

In the production of a pressure-adhesive layer an intrinsically non-tacky polymer may be tackified by the adding of a tackifying substance, e.g. plasticiser or other tackifying resin.

Examples of suitable tackifying resins are the terpene tackifying resins described in the periodical "Adhesives Age", Vol. 31, No. 12, November 1988, p. 28-29.

In the preferred case where the adhesive layer (c) is a thermal adhesive layer (or thermoadhesive layer, or TAL) it 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.

The (thermo)adhesive layer must be sufficiently thick so that most part of it remains intact after intense layer exposure. A thickness higher than 5 µm is preferred.

Having discussed the material elements of the thermal imaging medium for use in the present invention we shall now explain in detail the exposure and processing steps.

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 infrared 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).

Due to the intense laser radiation the adhesive strenght of the (thermo)adhesive layer towards the image forming layer is lowered to a value below the adhesive strenght of this image forming layer towards the support. In this way the image forming layer is image-wise released from the top adhesive layer.

After the laser exposure step a stripping sheet is laminated on top of the (thermo)adhesive layer. When this cleaning foil is transparent it may be composed of any of the same polymeric resins suitable for use as support. As for the support (a) 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. The stripping sheet may also be an opaque paper sheet.

Lamination may be conducted by putting the two materials in contact and then introducing the materials into the nip of a pair of laminating rollers under suitable pressure. When layer (c) is thermoadhesive suitable laminating temperatures usually range from approximately 60°C to 100°C, preferably from 70°C to 90°C.

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 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 contact material.

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

EXAMPLES

EXAMPLE 1

A thermal imaging medium was prepared as follows. Onto an unsubbed polyethylene terephthalate support having a thickness of 100 μm a carbon black containing image forming layer (C-layer) was coated from an aqueous medium. On top of this layer a thermoadhesive layer (TAL) was coated. The composition of both layers after drying is represented in table 1.

TABLE 1

layer	composition	amount (g/m^2)
TAL	BAYSTAL KA8522*	25
C-layer	carbon black (CORAX L6)	1.0
"	copoly(EA-MMA-MAA)**	0.8
"	ULTRAVON W***	0.4

* : copoly(styrene-butadiene-acrylic acid ; 60 % / 30 % / 10 %) (Bayer AG) ;
** : copoly(ethylacrylate-methylmethacrylate-methylacrylic acid ; 60 % / 23 % /17 %) ;
*** : commercial wetting agent (Ciba-Geigy) ;

This thermal imaging medium was exposed information-wise 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 paper stripping sheet (Ideal Brillant Blanc Paper) 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. The exposed areas of the carbon layer adhered to the original support giving rise there to a negative heat mode image while the unexposed aeras of the carbon layer were removed together with the thermoadhesive layer and the stripping sheet.

The Dmax values in the full areas of the obtained negative image were 4.5 (visual filter) and 5.0 (UV filter). The Dmin values were 0.05 (visual) and 0.07 (UV). A resolution up to a 10 µm dot could be obtained.

EXAMPLE 2

This example was similar to the previous one with the exception that the stripping sheet was a subbed polyethylene terephthalate foil having a thickness of 100 µm. A heat mode image with similar good properties as in the previous example was obtained.

EXAMPLE 3

This example was similar to example 2 with the exception that the carbon layer was coated from an organic solvent namely methylethylketone. The composition of the thermal imaging medium is represented in table 2.

TABLE 2

layer	composition	amount (g/m^2)
TAL	BAYSTAL KA8522	25
C-layer	carbon black (SPEZIAL SCWARZ)	1.0
"	nitrocellulose (E950)	0.5
"	solsperse disp. 5000 (?)	0.02
"	solsperse disp. 28000 (?)	0.08

A similar good heat mode image as in the previous examples was obtained.

Claims

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

(1) providing a thermal imaging medium comprising :

(a) a support,
(b) an image forming layer containing a binder, an image forming substance and a radiation to heat converting substance, which can be the same as or different from the image forming substance,
(c) an adhesive or thermoadhesive layer transparent for laser radiation, wherein the adhesive force between said (thermo)adhesive layer and said image forming layer is larger than the adhesive force between said image forming layer and said support,

(2) exposing information-wise by laser radiation through the side coated with (b) and (c) said thermal imaging medium whereby the adhesive force between said (thermo)adhesive layer and said image forming layer is lowered to a value smaller than that of the adhesive force between said image forming layer and said support,
(3) laminating a stripping sheet on top of said thermal imaging medium, and delaminating, whereby the unexposed areas are removed with the (thermo)adhesive layer and the stripping sheet thus forming a positive image on said stripping sheet, while the exposed areas remain adhered to said support thus forming a negative image on said support.

2. Method according to claim 1 wherein said image forming substance is a pigment.

3. Method according to claim 2 wherein said pigment is carbon black, being at the same time said radiation to heat converting substance.

4. Method according to any of claims 1 to 3 wherein the binder of said image forming layer is nitrocellulose.

5. Method according to any of claims 1 to 4 wherein said layer (c) is a thermoadhesive layer and contains a styrene-butadiene copolymer as thermoadhesive substance.

6. Method according to any of claims 1 to 5 wherein said (thermo)adhesive layer has a thickness of at least 5 μm.

7. Method according to any of claims 1 to 6 wherein said support (a) is a polyethylene terephthalate support.

8. Method according to any of claims 1 to 7 wherein said information-wise exposure by laser radiation is performed by means of an infra-red laser.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0410

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)
X	WO-A-94 12353 (POLAROID CORPORATION) * page 7, line 23 - page 8, line 16 * * page 9, line 15 - page 11, line 30 * * page 28, line 1 - page 30, line 23 * * claims 1-20; figures 1,5 * ---	1-8	B41M5/38 B41M5/40
X	US-A-5 340 693 (H.UYTTERHOEVEN ET AL.) * column 2, line 45 - column 4, line 26 * * claims 7-11; figures 1-3 * ---	1-8	
X	RESEARCH DISCLOSURE, no. 374, June 1995, HAVANT GB, pages 378-383, XP000519431 J.LAMOTTE ET AL.: ""Improved Thermal Imaging Medium"" * page 379, line 15 - line 43 * * page 380, line 10 - line 30 * * page 382, line 14 - line 25 * ---	1-8	
X,D	WO-A-95 00342 (AGFA-GEVAERT N.V.) * page 2, line 25 - page 3, line 18 * * page 6, line 22 - page 7, line 5 * * page 8, line 1 - line 27 * * claims 13-17 * ---	1-8	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** B41M
X,D	WO-A-93 03928 (E.I. DU PONT DE NEMOURS AND COMPANY) * page 2, line 14 - page 3, line 31 * * page 5, line 10 - line 21 * * page 8, line 28 - line 33 * * page 17, line 28 - page 18, line 27 * * claims 20-23 * --- -/--	1-8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 July 1996	Bacon, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

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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)
X,D	WO-A-88 04237 (POLAROID CORPORATION) * page 4, line 31 - page 5, line 15 * * page 6, line 21 - page 7, line 26 * * page 12, line 12 - line 20 * * page 17, line 27 - page 19, line 23 * * claims 1,4,17,18,36,37; figures 3,5 * -----	1-8	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

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THE HAGUE	5 July 1996	Bacon, A

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