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(54) **Laser absorbable photobleachable compositions**

Laser absorbierende ausbleichbare Zusammensetzungen

Compositions photoblanchissables, absorbant des lasers

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(73) Proprietor:
MINNESOTA MINING AND MANUFACTURING COMPANY
St. Paul, Minnesota 55133-3427 (US)

(72) Inventors:
- **Patel, Ranjan C.**
  Little Hallingbury, Essex CM22 2PP (GB)
- **Mott, Andrew W.**
  Bishops Stortford, Herts. (GB)
- **Nairne, Robert J.D.**
  Bishops Stortford, Herts. CM23 4EJ (GB)

(74) Representative:
Bowman, Paul Alan et al
LLOYD WISE, TREGEAR & CO.,
Commonwealth House,
1-19 New Oxford Street
London WC1A 1LW (GB)

(56) References cited:
EP-A- 0 403 157
EP-A- 0 518 470
EP-A- 0 602 893
EP-A- 0 675 003
US-A- 5 219 703

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EP 0 738 609 B1

Description

The invention relates to heat-sensitive imaging media which are imageable by laser address.

Many heat sensitive imaging media which are imageable by laser address comprise a photothermal converter, which converts laser radiation to heat, the heat being used to trigger the imaging process. IR- emitting lasers such as YAG lasers and laser diodes, are most commonly used for reasons of cost, convenience and reliability. Therefore, IR-absorbing dyes and pigments are most commonly used as the photothermal converter, although address at shorter wavelengths, in the visible region, is also possible as described in Japanese Patent Publication No. 51-88016.

Of particular interest are laser addressable thermal media giving rise to colour images. The best-known of these are the various forms of thermal transfer imaging in which a colourant is transferred from a donor to a receptor in response to heat generated from laser irradiation, including dye diffusion transfer (as described in US-A- 5,126,760), mass transfer of dyed or pigmented layers (as described in JP 63-319192) and ablation transfer of dyes and pigments (as described in US-A-5,171,650 and WO90/12342). Other types of laser thermal colour imaging media include those based on the formation or destruction of coloured dyes in response to heat (US-A-4602263), those based on the migration of toner particles into a thermally-softened layer (WO93/04411) and various peel-apart systems wherein the relative adhesion of a coloured layer to a substrate and a coversheet is altered by heat (WO93/03928, WO88/04237, DE4209873).

A problem common to all of these media is the possibility of contamination of the final image by the laser absorber. For example, in the case of thermal transfer media, the absorber may be co-transferred with the colourant. Unless the cotransferred absorber has absolutely no absorption bands in the visible part of the spectrum, the colour of the image will be altered. Various attempts have been made to identify IR dyes with minimal visible absorption (e.g., EP-A-0157568), but in practice the IR absorption band nearly always tails into the visible region, leading to contamination of the image.

A number of methods have been proposed to remove contamination by the absorber of the final image. For example EP-A-0675003 describes contacting the transferred image of laser thermal transfer imaging with a thermal bleaching agent capable of bleaching the absorber. This method complicates the imaging process and it has not been possible to bleach certain dyes, for example, Cyasorb 165™ (American Cyanamid) which is commonly used with YAG-lasers. WO93/04411 and US-A-5219703 disclose an acid-generating compound which bleaches the IR absorbing dye. However, an additional UV exposure is generally required (optionally in the presence of a UV absorber), again complicating the imaging process.

There is a need for improved methods of bleaching the IR absorbing dye in laser addressed thermal media.

Photoredox processes involving dyes have been disclosed in the art. A photoexcited dye may accept an electron from a coreactant, the dye acting as a photo-oxidant. There are a number of examples where this type of process has been used, although not in the context of laser-addressable thermal imaging media. In particular, there are a number of systems comprising a cationic dye in reactive association with an organoborate ion (see US-A-5329300, US-A-5166041, US-A-4447521, US-A-4343891 and J. Chem Soc. Chem Commun 1993 299). After transferring an electron to the excited dye, organoborate ions fragment into free radicals which may initiate polymerisation reactions (J. Am. Chem. Soc. 1985 (110) 2326-8) or may react further and thus form an image (US-A-4447521 and US-A-4343891).

Another example of imaging involving photoreduction of a dye is disclosed in US-A-4816379. This describes media comprising a photocurable layer containing a UV photoinitiator and photopolymerisable compounds, the layer additionally comprising a cationic dye of defined structure and a mild reducing agent capable of reducing said dye in its photoexcited state. Imagewise exposure at a wavelength absorbed by the cationic dye causes photoreduction of same and generation of a polymerisation inhibitor, so that a subsequent uniform UV exposure gives polymerisation only in the previously unexposed areas. Conventional wet development leaves a positive image. The cationic dyes are described as visible-absorbing, and are of a type not known to be IR-absorbing. Shifts in the absorbance of the cationic dyes (including bleaching) are noted. The preferred reducing agents are salts of N-nitrosocyclohexylhydroxylamine, but other possibilities include ascorbic acid and thiourea derivatives. There is no disclosure of thermal imaging media.

J. Imaging Sci. & Technol 1993 (37), 149-155 describes the photoreductive bleaching of pyrylium dyes by allylthiourea derivatives under conditions of UV flood exposure.

EP-A-O515133 and J. Org. Chem 1993 (58), 2614-8 disclose the photoreduction of neutral xanthene dyes by amines and other electron donors, for initiation of polymerisation and in photosynthetic applications.

The ability of dihydropyridine derivatives to transfer an electron to a photoexcited Ru(III) complex is disclosed in J. Amer. Chem. Soc 1981 (103), 6495-7. The reactions were carried out in solution and were not used for imaging purposes.

In a first aspect of the invention there is provided a laser addressable thermal imaging medium comprising a photothermal converting dye in association with a heat-sensitive imaging system and a photoreducing agent, said photoreducing agent bleaching said dye during laser address of the medium.

"Laser-addressable thermal imaging media" refers to imaging media in which an image forms in response to heat,

said heat being generated by absorption of coherent radiation (as is emitted by lasers, including laser diodes). Preferably, the image formed is a colour image, and in preferred embodiments the thermal imaging medium is a colourant donor medium.

To be able to function in this way, the media must comprise a "photothermal converter", i.e., a substance which absorbs incident radiation with concomitant generation of heat. When a dye absorbs radiation, a proportion of its molecules are converted to an electronically excited state, and the basis of photothermal conversion is the dissipation of this electronic excitation as vibrational energy in the surrounding molecules, with the dye molecules reverting to the ground state. The mechanism of this dissipation is not well understood, but it is generally believed that the lifetime of the excited state of the dye is very short (e.g. of the order of picoseconds, as described by Schuster et al., J.Am.Chem.Soc 1990 (112), 6329). Thus, in the absence of competing processes, a dye molecule might experience many excitation-deexcitation cycles during even the shortest laser pulses normally encountered in laser thermal imaging (of the order of nanoseconds).

Possible competing processes include photoredox processes in which the photo-excited dye molecules donate or accept an electron to or from a reagent in its ground state. This may initiate further chemical transformations which destroy the dye's ability to undergo further excitation-deexcitation cycles. Of particular relevance to the present invention are photoreduction processes, in which it is believed a suitable reducing agent donates an electron to fill the vacancy caused in the dye's lower energy orbitals when an electron is promoted to a higher energy orbital by photoexcitation. The process is believed to occur most readily in the case of cationic dyes (which have a positive charge associated with the chromophore), but also has been observed in the case of neutral dyes such as xanthenes (see US-A-4816379, EP-A-0515133) but not in the context of thermal imaging media. In the present context, the process provides a convenient and effective method of bleaching a laser-absorbing dye without, surprisingly, significantly affecting the dye's ability to act as a photothermal converter.

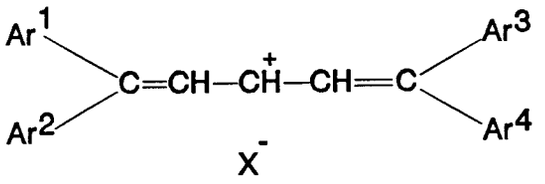
In the prior art, the problem of bleaching a laser-absorbing dye has been tackled by causing the dye to react with a bleaching agent subsequent to its fulfilment of the photothermal conversion role, but in the present invention bleaching occurs when the dye is in its excited state, i.e. when it is in the process of fulfilling its photothermal conversion role. This might have been expected to seriously impair the photothermal conversion effect, but in practice there is little or no reduction in sensitivity. What is apparently obtained is a more controlled generation of heat, with less tendency for "runaway" temperature rises which may lead to indiscriminate vapourisation of the media. If milder imaging processes are desired, such as melt-stick transfer, where it is desirable to preserve the integrity of the media, this effect is highly beneficial.

"Bleaching" in the context of this invention means an effective diminution of absorption bands giving rise to visible colouration by the photothermal converting dye. Bleaching may be achieved by destruction of the aforementioned absorption bands, or by shifting them to wavelengths that do not give rise to visible colouration.

Depending on the choice of photoreducing agent, dyes suitable for use in the invention include cationic dyes such as polymethine dyes, pyrylium dyes, cyanine dyes, diamine dication dyes, phenazinium dyes, phenoxazinium dyes, phenothiazinium dyes, acridinium dyes, and also neutral dyes such as the xanthene dyes disclosed in EP-A-O515133 and squarylium dyes. Preferred dyes have absorption maxima that match the output of the laser sources most commonly used for thermal imaging such as laser diodes and YAG lasers. Absorption in the range 600 - 1500nm is preferred, and in the range 700 - 1200nm is most preferred.

Preferred classes of cationic dyes for use in the invention include the tetraarylpolymethine (TAPM) dyes. These generally absorb in the 700 - 900nm region, making them suitable for diode laser address, and there are several references in the literature to their use as absorbers in laser address thermal transfer media, e.g. JP-63-319191, JP-63-319192 and US-A-4950639. When these dyes are co-transferred with the colourant, a blue cast is given to the transferred image because the TAPM dyes generally have absorption peaks which tail into the red region of the spectrum. European Patent Application No. EP-A-675003 describes the thermal bleaching of TAPM dyes in the thermal transfer media via the provision of thermal bleaching agents in the receptor layer (EP-A 0 675 003 constitutes prior art according to Article 54(3)(4) EPC). It has now been found that TAPM dyes can bleach cleanly by a photoreductive process as described in the present invention.

The general formula for TAPM dyes is disclosed in US-A-5135842. Preferred examples have a nucleus of general formula I:-



in which:

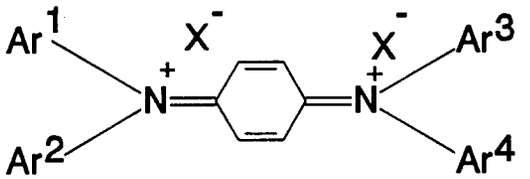
Ar^1 - Ar^4 are aryl groups which may be the same or different such that at least two of Ar^1 - Ar^4 have a tertiary amino group in the 4-position, and X is an anion.

Examples of tertiary amino groups include dialkylamino groups, diarylamino groups, and cyclic substituents such as pyrrolidino, morpholino, piperidino. The tertiary amino group may form part of a fused ring system, e.g., one or more of Ar^1 - Ar^4 may represent a julolidine group.

Preferably the anion X is derived from a strong acid (e.g., HX should have a pKa of less than 3, preferably less than 1). Suitable identities for X include ClO_4, BF_4, CF_3SO_3, PF_6, AsF_6, SbF_6.

A preferred dye of Formula I has $Ar^1 = Ar^3$ = 4-dimethylaminophenyl and $Ar^2 = Ar^4$ = phenyl and X = CF_3SO_3.

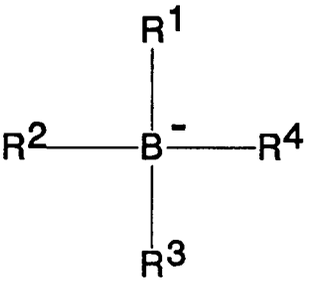
Another preferred class of cationic dye is amine cation radical dyes, also known as immonium dyes, described for example in WO90/12342 and JP51-88016. These include diamine di-cation dyes, exemplified by the commercially available Cyasorb IR165 (American Cyanamid), which have a nucleus of general formula II :-



in which Ar^1 - Ar^4 and X are as defined above. Although these dyes show peak absorptions at relatively long wavelengths (ca.1050nm, suitable for YAG laser address), the absorption band is broad and tails into the red region. EP-A-0675003 teaches that partial bleaching of diamine di-cation dyes is possible through a thermal process, but it has now been found that total bleaching may be achieved by a photoreductive process.

The reducing agent used in the invention may be any compound or group capable of interacting with the photothermal converting dye and bleaching the same under the conditions of photoexcitation and high temperature associated with laser address of thermal imaging media, but must not react with the dye in its ground state under normal storage conditions. The reducing agent acts as a photoreductant towards the dye, i.e. it transfers an electron only to the photoexcited form of the dye, so that the composition is stable in the absence of photoexcitation. The choice of reducing agent may depend on the choice of laser-absorbing dye. Candidate combinations of dye and reducing agent may be screened for suitability by coating mixtures of dye and reducing agent (optionally in a mutually compatible binder) on a transparent substrate, and thereafter monitoring the effect on the absorption spectrum of the dye of (a) storage of the coating in the dark at moderately elevated temperatures for several days, and (b) irradiation of the coating at the absorption maximum of the dye by a laser source. For a suitable combination, conditions (a) should have minimal effect and conditions (b) should bleach the dye.

Reducing agents suitable for use in the invention are generally good electron donors, i.e., have a low oxidation potential (Eox), typically less than 1.0V, and preferably not less than 0.40V. Depending on the choice of photothermal converting dye, they may be neutral molecules or anionic groups. Examples of anionic groups include the salts of N-nitrosocyclohexylhydroxylamine disclosed in US-A-4816379, N-phenylglycine salts and organoborate salts comprising an anion of formula III :-



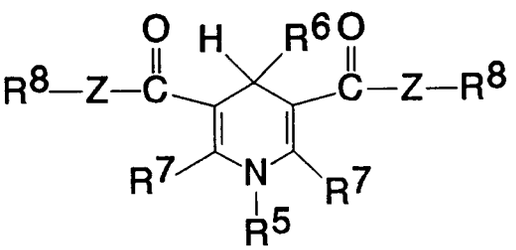
in which:

R^1 - R^4 independently represent alkyl, aryl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, alicyclic or saturated or unsaturated heterocyclic groups, including substituted derivatives of these groups, with the proviso that at least one of R^1 - R^4 is an alkyl group of up to 8 carbon atoms.

US-A-5166041 describes the photobleaching of a variety of IR-absorbing cationic dyes by such species, but not in the context of laser addressed thermal imaging. Likewise, photobleaching of visible-absorbing cyanine dyes by alkylborate ion is described in US-A-4,447,521, US-A- 4,343,891. Anionic reducing agents may be formulated as the counterion to the cationic dye.

Neutral reducing agents suitable for use in the invention generally (but not necessarily) possess one or more labile hydrogen atoms or acyl groups which may be transferred to the dye subsequent to electron transfer, hence effecting irreversible bleaching of the dye. Examples of neutral reducing agents include the thiourea derivatives mentioned in US-A-4816379, ascorbic acid, benzhydrols, phenols, amines and leuco dyes (including acylated derivatives thereof). It is highly desirable that the photo-oxidation products of the reducing agent should not themselves be visibly coloured. Surprisingly, in certain cases it has been found possible to employ leuco dyes as reducing agents without generating unwanted colouration.

A preferred class of reducing agent comprises the 1,4-dihydropyridine derivatives having a nucleus of general formula IV :-



in which:

R^5 is selected from H, alkyl, aryl, alicyclic or heterocyclic groups;
R^6 is an aryl group;
each R^7 each R^8 is independently selected from alkyl, aryl, alicyclic and heterocyclic groups, and
Z represents a covalent bond or an oxygen atom.

"Alkyl" refers to alkyl groups of up to 20 preferably up to 10, and most preferably lower alkyl, meaning up to 5 carbon atoms.

"Aryl" refers to aromatic rings or fused ring systems of up to 14, preferably up to 10, most preferably up to 6 carbon atoms.

"Alicyclic" refers to non-aromatic rings or fused ring systems of up to 14, preferably up to 10, most preferably up to 6 carbon atoms.

"Heterocyclic" refers to aromatic or non-aromatic rings or fused ring systems of up to 14, preferably up to 10, most

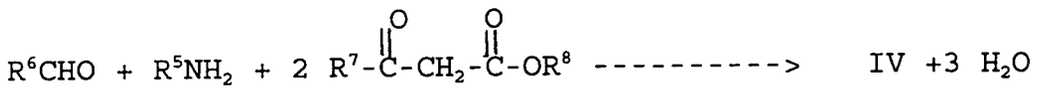
preferably up to 6 atoms selected from C, N, 0 and S. As is well understood in this technical area, a large degree of substitution is not only tolerated, but is often advisable. As a means of simplifying the discussion, the terms, "nucleus", "groups" and "moiety" are used to differentiate between chemical species that allow for substitution or which may be substituted and those which do not or may not be so substituted. For example, the phrase "alkyl group" is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, octyl, cyclohexyl, iso-octyl, t-butyl and the like, but also alkyl chains bearing conventional substitutents known in the art, such as hydroxyl, alkoxy, phenyl, halogen (F, Cl, Br and I), cyano, nitro, amino etc. The term "nucleus" is likewise considered to allow for substitution. The phrase "alkyl moiety" on the other hand is limited to the inclusion of only pure hydrocarbon alkyl chains, such as methyl, ethyl, propyl, cyclohexyl, iso-octyl, t-butyl etc.

Compounds of formula IV are found to bleach cationic dyes (particularly those of formulae I and II) rapidly and cleanly when the latter are photoexcited, but are stable towards the dyes at room temperature in the dark. Furthermore, they are readily synthesised, stable compounds and do not give rise to coloured degradation products, and so are well suited for use in media that generate coloured images.

Therefore, in a further aspect of the present invention, there is provided a method of bleaching a cationic dye by photoirradiating a cationic dye to an electronically excited state in the presence of a compound having a nucleus of general formula IV.

In formula IV, Z is preferably an oxygen atom, R^5 is preferably H or phenyl (optionally substituted), R^6 is preferably phenyl (optionally substituted), R^7 is preferably lower alkyl (esp. methyl) and R^8 is preferably lower alkyl (e.g., ethyl).

Compounds of formula IV may be synthesised by co-condensation of an aldehyde, an amine and two equivalents of a beta-ketoester in an adaptation of the well known Hantsch pyridine synthesis:-



The compound of formula IV or other reducing agent is typically coated in the same layer or layers as the dye, but may additionally or alternatively be present in one or more separate layers, provided that reactive association of the dye and reducing agent is possible during the photoirradiation. Absorption of laser pulses can cause extremely rapid rises in temperature and pressure, which may readily enable the ingredients of two or more adjacent layers to mix and interact.

Preferably at least one mole of reducing agent is present per mole of dye, but more preferably an excess is used, e.g., in the range of 5 - 50-fold. In the case of compounds of Formula IV, a metal salt stabiliser may be incorporated, e.g., a magnesium salt, as this has been found to improve the thermal stability of the system without affecting the photoactivity. Quantities of about 10 mole% based on the compound of formula IV are effective.

The laser-addressable thermal imaging media may comprise any imaging media in which photothermal conversion is used to generate an image, but the invention finds particular use with media which generate a colour image which may be altered by the presence of unbleached photothermal converting dye. Such media may take several forms, such as colourant transfer systems, peel-apart systems, phototackification systems and systems based on unimolecular thermal fragmentations of specific compounds.

Preferred laser addressable thermal imaging media include the various types of laser thermal transfer media. In these systems, a donor sheet comprising a layer of colourant and a suitable absorber is placed in contact with a receptor and the assembly exposed to a pattern of radiation from a scanned laser source. The radiation is absorbed by the absorber, causing a rapid buildup of heat in the exposed areas of the donor which in turn causes transfer of colourant from those areas to the receptor. By repeating the process with one or more different-coloured donors, a multicolour image can be assembled on a common receptor. The system is particularly suited to the colour proofing industry, where colour separation information is routinely generated and stored electronically, and the ability to convert such data into hardcopy via digital address of "dry" media is particularly advantageous.

The heat generated may cause colourant transfer by a variety of mechanisms. For example, there may be a rapid build up of pressure as a result of decomposition of binders or other ingredients to gaseous products, causing physical propulsion of colourant material to the receptor ("ablation transfer") , as described in US-A-5171650 and WO90/12342. Alternatively, the colourant and associated binder materials may transfer in a molten state ("melt-stick transfer"), as described in JP63-319191. Both of these mechanisms produce mass transfer, i.e. there is essentially 0% or 100% transfer of colourant depending on whether the applied energy exceeds a certain threshold. A somewhat different mechanism is diffusion or sublimation transfer, whereby a colourant is diffused (or sublimed) to the receptor without co-transfer of binder. This is described, for example, in US-A-5126760, and enables the amount of colourant transferred to vary continuously with the input energy.

Any of the donor element constructions known in the art of laser thermal transfer imaging may be used in the present invention. Thus, the donor may be adapted for sublimation transfer, ablation transfer, or melt-stick transfer. Typically, the donor element comprises a substrate (such as polyester sheet), a layer of colourant, a dye (preferably cationic) as photothermal converter and a reducing agent. The dye and reducing agent may be in the same layer as the colourant, in one or more separate layers, or both. Other layers may be present, such as dynamic release layers as taught in US-A-5171650. Alternatively, the donor may be self-sustaining, as taught in EP-A-0491564. The colourant generally comprises one or more dyes or pigments of the desired colour dissolved or dispersed in a binder, although binder-free colourant layers are also possible, as taught in WO-A 94/04368 (= EP-A 0 655 033). Preferably the colourant comprises dyes or pigments that reproduce the colours shown by standard printing ink references provided by the International Prepress Proofing Association, known as SWOP colour references.

Particularly preferred donor elements are of the type described in EP-A-0602893 in which the colourant layer comprises a fluorocarbon compound in addition to pigment and binder. The receptor elements used in the present invention are entirely conventional. Thus, they typically comprise a substrate such as paper or plastic sheet optionally bearing one or more resin coatings. The choice of the resin for the receptor layer (e.g. in terms of Tg, softening point, etc.) may depend on the type of transfer involved (ablation, melt-stick, or sublimation), but for use with the preferred donor elements, Butvar™ B76 polyvinyl butyral (Monsanto), polyvinyl resins, and similar thermoplastic materials are highly suitable.

The procedure for imagewise transfer of colourant from donor to receptor is entirely conventional. The two elements are assembled in intimate face-to-face contact, e.g., by vacuum draw down, or alternatively by means of cylindrical lens apparatus as described in US-A-5475418, and scanned by a suitable laser. The assembly may be imaged by any of the commonly-used lasers, depending on the absorber used, but address by near infrared and infrared emitting lasers such as diode lasers and YAG lasers, is preferred. Best results are obtained from a relatively high intensity laser exposure, e.g., of at least 10^{23} photons/cm^2/sec. For a laser diode emitting at 830nm, this corresponds approximately to an output of 0.1W focused to a 20 micron spot with a dwell time of approximately 1 microsecond. In the case of YAG laser exposure at 1064nm, a flux of at least $3X10^{24}$ photons/cm^2/sec is preferred, corresponding roughly to an output of 2W focused to a 20 micron spot, with a dwell time of approximately 0.1 microsecond.

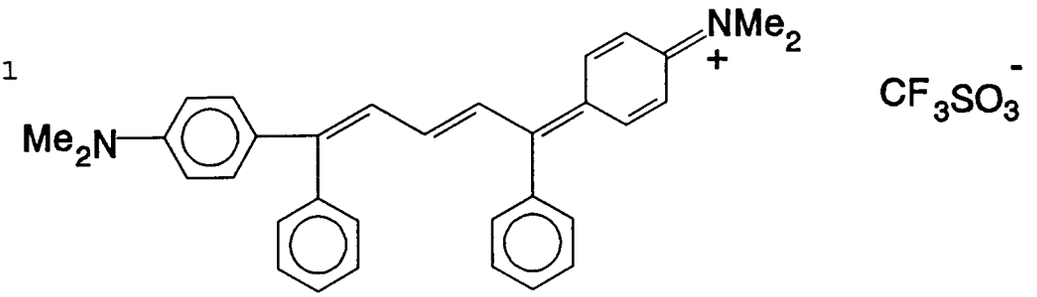
Any of the known scanning devices may be used, e.g., flat-bed scanners, external drum scanners or internal drum scanners. In these devices, the assembly to be imaged is secured to the drum or bed (e.g., by vacuum draw-down) and the laser beam is focused to a spot (e.g., of about 10-25, preferably about 20 microns diameter) on the IR-absorbing layer of the donor. This spot is scanned over the entire area to be imaged while the laser output is modulated in accordance with electronically stored image information. Two or more lasers may scan different areas of the donor-receptor assembly simultaneously, and if necessary, the output of two or more lasers may be combined optically into a single spot of higher intensity. Laser address is normally from the donor side, but may alternatively be from the receptor side if the receptor is transparent to the laser radiation. Peeling apart the donor and receptor reveals a monochrome image on the receptor. The process may be repeated one or more times using donor sheets of different colours to build a multicolour image on a common receptor. Because of the interaction of the photothermal converting dye and reducing agent during laser address, the final image can be free from contamination by the photothermal converter. In some situations, the receptor to which the colourant image is initially transferred is not the final substrate on which the image is viewed. For example, US-A-5126760 describes thermal transfer of the image from the first receptor to a second receptor for viewing purposes.

An alternative type of laser addressable thermal imaging media suitable for use in the present invention is an adaptation of the migration imaging described in WO93/04411. As detailed therein, this involves deposition of marking particles as a substantially continuous layer on a thermoplastic imaging element and establishing an attraction between the two (e.g., by electrostatic charging). The particles, the thermoplastic imaging element, or both contain an IR absorbing dye such that when the assembly is imagewise exposed by a laser, softening of the thermoplastic element occurs, allowing the marking particles to migrate therein under the force of attraction and become embedded on subsequent cooling. Particles are removed from the non-image areas by wiping or other suitable means. An acid-generating compound, such as an iodonium salt, is incorporated in the particles, the thermoplastic element or both to enable bleaching of the IR dye either during laser address or (more effectively) by uniform UV exposure as an additional step. This type of media may be adapted to the present invention by use of a dye in the marking particles as laser absorber, with a reducing agent present in the particles and/or the thermoplastic element. Effective bleaching of the laser absorber is then possible without the need for further UV exposure. Other types of laser thermal colour imaging media within the scope of the present invention include those based on the formation or destruction of coloured dyes in response to heat (as described in US4602263), and various peel-apart systems wherein the relative adhesion of a coloured layer to a substrate and a coversheet is altered by heat (as described in WO93/03928, WO88/04237, DE4209873).

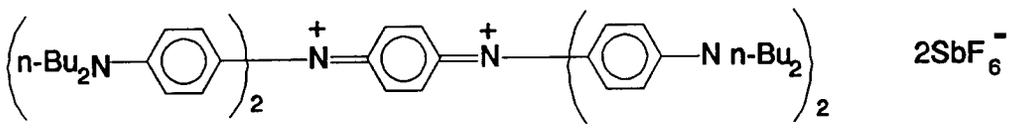
The invention is hereinafter described in more detail by way of reference only to the following Examples.

The following materials are used in the Examples:-

Dye 1

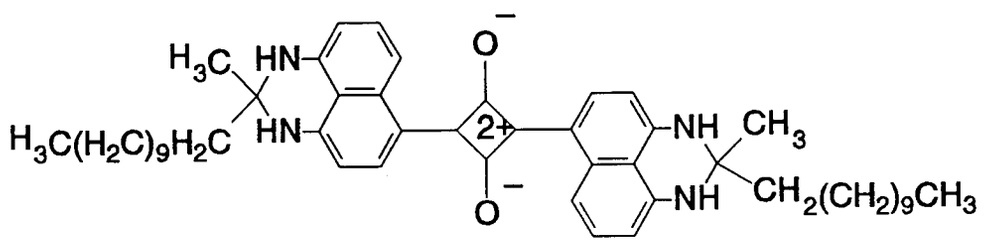


Dye 2

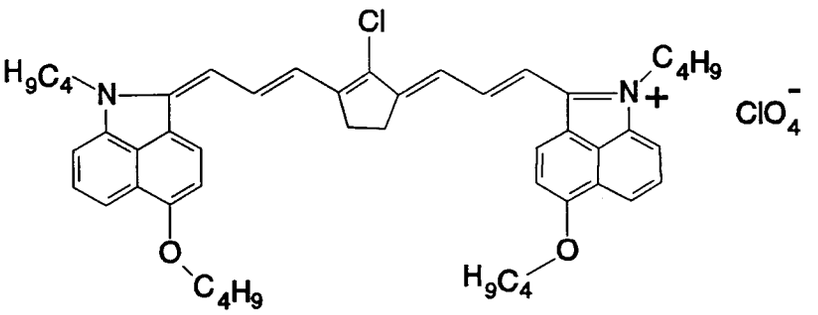


(Supplied under the trade name "Cyasorb IR165" by American Cyanamid).

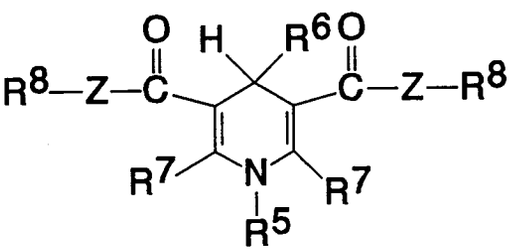
Dye 3



Dye 4

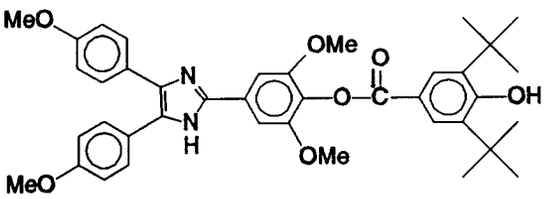


Donor 1(a)-1(d):-

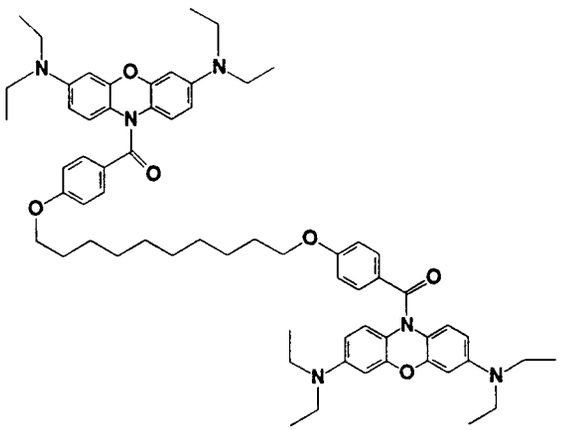


	R^5	R^6	R^7	R^8	Z
1(a)	H	Ph	Me	Et	O
1(b)	Ph	Ph	Me	Et	O
1(c)	H	3,4-$(OH)_2C_6H_4$	Me	Et	O
1(d)	H	Ph	Me	Me	-

Donor 2



Donor 3 - (EP-A-0681210)



Butvar™ B-76 - polyvinylbutyral (Monsanto).
VAGH and VYNS - vinyl copolymers resins supplied by Union Carbide
MEK - methyl ethyl ketone (2-butanone)
FC - N-methylperfluorooctanesulphonamide

Example 1

This example demonstrates the photoreductive bleaching of Dyes 1 and 2 by Donors 1 (a) and 2.
The following formulations were coated on 100 micron unsubbed polyester base at 12 micron wet thickness and air dried to provide Elements 1 - 4 :-

	Element 1	Element 2	Element 3	Element 4(c)
Butvar B76 (10%w/w in MEK)	2.75g	-	5.5g	5.5g
MEK	2.75g	5.5g	3.5g	3.5g
Ethanol	-	0.5g	-	-
Dye 1	0.08g	0.125g	-	-
Dye 2	-	-	0.25g	0.25g
Donor 1 (a)	0.4g	-	0.68g	-
Donor 2	-	0.10g	-	-

(c) = control (not in accordance with invention)

Elements 1 and 2 were pale blue/pink in appearance and Elements 3 and 4 pale grey. Samples measuring 5cm x 5cm were mounted on a drum scanner and exposed by a 20 micron laser spot scanned at various speeds. The source was either a laser diode delivering 115mW at 830nm at the image plane(Elements 1 and 2), or a YAG laser delivering 2W at 1068nm (Elements 3 and 4). The results are reported in the following table in which OD represents optical density:

	Element 1	Element 2
OD (830nm) (initial)	1.9	1.3
OD after 600cm/sec scan	1.7	1.2
OD after 400cm/sec scan	1.5	0.6
OD after 200cm/sec scan	0.7	0.3
	Element 3	Element 4(c)
OD (1100nm) (initial)	1.3	1.3
OD after 6400cm/sec scan	0.9	1.3
OD after 3200cm/sec scan	0.6	1.1

(c) = control (not in accordance with invention)

In the case of Elements 1 - 3, colourless tracks were formed in the exposed areas, with the degree of bleaching correlating with scan speed, whereas Element 4 (a control lacking a donor compound) showed negligible bleaching.

It is noteworthy that Donor 2, which may be regarded as an aroyl-protected leuco dye, did not give rise to any colouration attributable to the corresponding dye.

The preparation and imaging of Element 1 was repeated, substituting Donors 1(b) - 1(d) for Donor 1(a), giving similar results.

Example 2

This example demonstrates the photoreductive bleaching of Dyes 3 and 4 by Donor 3, which may be regarded as an acyl-protected leuco phenoxazine dye. Elements 5 and 6 were prepared in the same manner as Elements 1 - 4 from the following formulations:-

	Element 5	Element 6
MEK	4.0g	4.0g
Ethanol	0.3g	0.4g
Dye 3	0.08g	-
Dye 4	-	0.1g
Donor 3	0.05g	0.1g

Laser diode irradiation at a scan speed of 200cm/sec (as described in Example 1) produced the following changes in optical density:-

	OD change (670nm)	OD change (IR band)
Element 5	<0.1	-1.2
Element 6	<0.1	-0.8

Thus, efficient bleaching of the IR dye was observed, with no significant build up of dye density attributable to the phenoxazine dye corresponding to Donor 3.

Example 3

The example demonstrates thermal transfer media in accordance with the invention.

A millbase was prepared by dispersing 4g magenta pigment chips in 32g MEK using a McCrone Micronising Mill. The pigment chips were prepared by standard procedures and comprised blue shade magenta pigment and VAGH binder in a weight ratio of 3:2.

The following formulations were prepared and coated as described in Example 1 to give Elements 7 - 10 :-

	Element 7	Element 8(c)	Element 9	Element 10(c)
Millbase	5.5g	5.5g	5.5g	5.5g
MEK	2.0g	2.0g	2.0g	2.0g
Ethanol	1.0g	1.0g	1.0g	1.0g
Dye 1	0.125g	0.125g	-	-
Dye 2	-	-	0.2g	0.2g
Donor 1(a)	0.6g	-	0.6g	-
FC	0.025g	0.025g	0.025g	0.025g

(c) = control without donors (not in accordance with invention) (The FC was added after the other ingredients had been mixed for 30 minutes under low light conditions).

Samples of the resulting coatings were assembled in contact with a VYNS-coated paper receptor and mounted on an external drum scanner with vacuum hold-down, then addressed with a laser diode (830nm, 110mW, 20micron spot) scanned at 100 or 200 cm/sec. The receptor sheets, after peeling from the donors, showed lines of magenta pigment contaminated to varying extents by Dye 1 or Dye 2. The degree of contamination was assessed by measuring the reflection density of the transferred tracks at 830nm or 1050nm as appropriate:-

	200 cm/sec	100 cm/sec
Element 7	0.3	0.1
Element 8(c)	0.8	0.6
Element 9	0.8	0.4
Element 10(c)	1.5	1.4

(c) = control without donors (not in accordance with invention) (The FC was added after the other ingredients had been mixed for 30 minutes under low light conditions).

The elements of the invention show much reduced contamination by the IR dye, and purer magenta images were obtained.

Claims

1. A laser addressable thermal imaging element comprising a bleachable photothermal converting dye in association with a heat-sensitive imaging medium, and a photoreducing agent for said dye, said photoreducing agent bleaching said dye on laser address of the element.

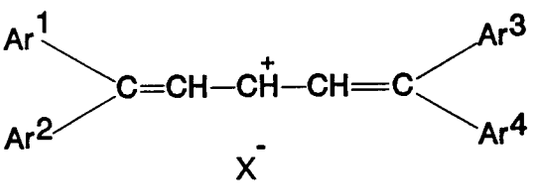
2. A thermal imaging element according to Claim 1 wherein said dye has an absorption maximum in the range of 600-1500nm.

3. A thermal imaging element according to Claim 1 or Claim 2 wherein said dye is a cationic dye or a neutral dye.

4. A thermal imaging element according to Claim 3 wherein said dye is selected from polymethine dyes, pyrylium dyes, cyanine dyes, diamine dication dyes, phenazinium dyes, phenoxazinium dyes, acridinium dyes, xanthene dyes and squarylium dyes.

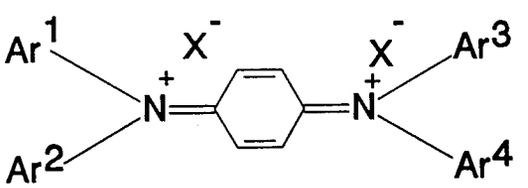
5. A thermal imaging element according to Claim 4 wherein said dye has the formula:-

(I)



or

(II)

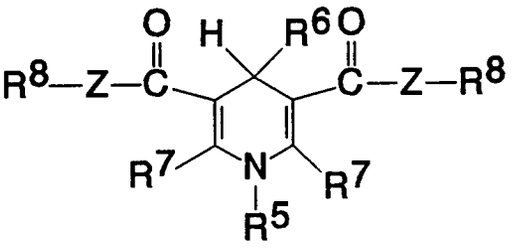


where Ar^1- Ar^4 independently represent aryl groups such that at least two of Ar^1 - Ar^4 have a tertiary amino group

in the 4 position and X is an anion.

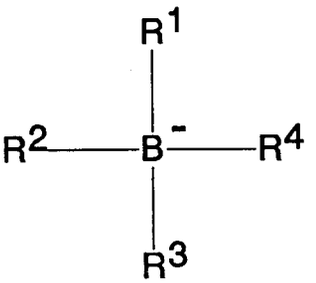
6. A thermal imaging element according to Claim 5 wherein said tertiary amino group is selected from dialkyl amino groups, diarylamino groups or cyclic substituents selected from pyrrolidino, morpholino, piperidino or forms part of a fused ring system and X is one of $Cl0_4$, BF_4, CF_3SO_3, PF_6, AsF_6 and SbF_6.

7. A thermal imaging element according to any preceding claim wherein the reducing agent is selected from compounds having a nucleus of the formula:-



wherein:

R^5 is selected from H, alkyl, aryl, alicyclic or heterocyclic;
R^6 represents an aryl group; each R^7 and each R^8 is independently selected from alkyl, aryl, alicyclic and heterocyclic, and Z represents a covalent bond or an oxygen atom; and
salts of N-nitrosocyclohexylhydroxylamine, N-phenylglycine and organoborate salts comprising an anion of formula:



in which R^1 - R^4 independently represent alkyl, aryl, alkaryl, aralkyl, alkenyl, alkynyl, silyl, alicyclic or saturated or unsaturated heterocyclic groups, including substituted derivatives of these groups with the proviso that at least one of R^1 - R^4 is an alkyl group of up to 8 carbon atoms; and neutral reducing agents possessing one or more labile hydrogen atoms or acyl groups.

8. A thermal imaging element according to Claim 7 wherein R^5 is H or phenyl group, R^6 is phenyl group, R^7 and R^8 are lower alkyl.

9. A thermal imaging element according to Claim 7 wherein said neutral reducing agent is selected from thiourea derivatives, ascorbic acid, benzhydrols, phenols, amines and leuco dyes and acylated derivatives thereof.

10. A thermal imaging element according to any preceding claim wherein at least one mole of reducing agent is present per mole of dye.

11. A thermal imaging element according to any one of Claims 1 to 7 comprising one of the following combinations of photoconverting dye and photoreducing agent:

(i) a dye of formula (I) or formula (II) as defined in Claim 5 and a reducing agent of formula (IV) as defined in

Claim 7;

(ii) a cationic dye and a reducing agent of formula (III) as defined in Claim 7; and
(iii) a cyanine or squarylium dye and an acyl protected leuco dye.

12. A thermal imaging element according to any preceding claim wherein said element is a colourant transfer system, a peel-apart system, a phototackification system or a unimolecular thermal fragmentation system.

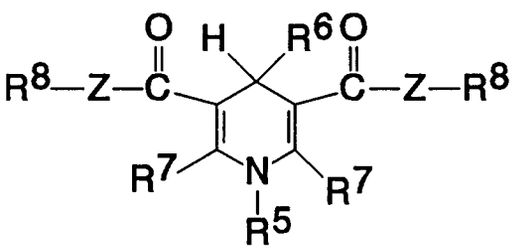
13. A thermal imaging element as claimed in Claim 12 in the form of a colourant transfer donor which comprises pigment particles dispersed in a binder.

14. A thermal imaging element as claimed in Claim 13 which additionally comprises a fluorocarbon.

15. A method of imaging which comprises the step of exposing a thermal imaging element according to any preceding claim to laser irradiation at a wavelength absorbed by said photothermal converting dye, under exposure conditions such that absorption by said dye generates sufficient heat for imaging of said heat-sensitive imaging medium, and said reducing agent bleaches said dye.

16. A method as claimed in Claim 15 wherein the thermal imaging element comprises a colourant transfer system, a peel-apart system, a phototackification system or a unimilecular thermal fragmentation system.

17. A method of bleaching a cationic dye comprising photoirradiating said dye to an electronically excited state in the presence of a 1,4 dihydropyridine having a nucleus of general formula IV:-



wherein:

R^5 is selected from H, alkyl, aryl, alicyclic and heterocyclic;
R^6 represents an aryl group; and
each R^7 and each R^8 is independently selected from alkyl, aryl, alicyclic heterocyclic, and Z represents a covalent bond or an oxygen atom.

Patentansprüche

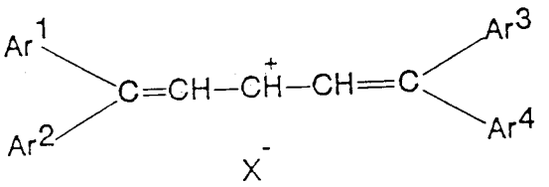
1. Laseransprechbares thermisches Bildaufzeichnungselement, umfassend einen bleichbaren photothermischen Konversionsfarbstoff in Kombination mit einem wärmeempfindlichen Bildaufzeichnungsmedium und ein Photoreduktionsmittel für den Farbstoff, wobei das Photoreduktionsmittel den Farbstoff ausbleicht, wenn das Element von einem Laser angesprochen wird.

2. Thermisches Bildaufzeichnungselement gemäß Anspruch 1, wobei der Farbstoff ein Absorptionsmaximum im Bereich von 600 bis 1500 nm aufweist.

3. Thermisches Bildaufzeichnungselement gemäß Anspruch 1 oder 2, wobei der Farbstoff ein kationischer Farbstoff oder ein neutraler Farbstoff ist.

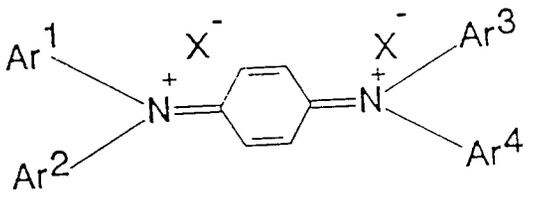
4. Thermisches Bildaufzeichnungselement gemäß Anspruch 3, wobei der Farbstoff ausgewählt ist aus Polymethinfarbstoffen, Pyryliumfarbstoffen, Cyaninfarbstoffen, Diamindikationfarbstoffen, Phenazinfarbstoffen, Phenoxazinfarbstoffen, Acridinfarbstoffen, Xanthenfarbstoffen und Quadratsäurefarbstoffen.

5. Thermisches Bildaufzeichnungselement gemäß Anspruch 4, wobei der Farbstoff die Formel:



(I)

oder

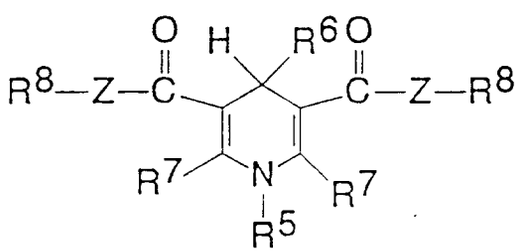


(II)

aufweist, wobei Ar^1 bis Ar^4 unabhängig voneinander Arylreste darstellen, so daß mindestens zwei aus Ar^1 bis Ar^4 eine tertiäre Aminogruppe in Position 4 besitzen und wobei X ein Anion ist.

6. Thermisches Bildaufzeichnungselement gemäß Anspruch 5, wobei die tertiäre Aminogruppe aus Dialkylaminogruppen, Diarylaminogruppen oder cyclischen Substituenten, ausgewählt aus Pyrrolidino-, Morpholino- oder Piperidinogruppen ausgewählt ist oder einen Teil eines kondensierten Ringsystems darstellt und wobei X ClO_4, BF_4, CF_3SO_3, PF_6, AsF_6 oder SbF_6 ist.

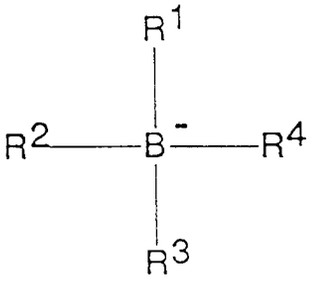
7. Thermisches Bildaufzeichnungselement gemäß einem der vorstehenden Ansprüche, wobei das Reduktionsmittel ausgewählt ist aus Verbindungen mit einem Kern der Formel



(IV)

wobei:

R^5 ausgewählt ist aus H, Alkyl-, Aryl-, alicyclischen oder heterocyclischen Resten;
R^6 einen Arylrest darstellt;
R^7 und R^8 jeweils unabhängig voneinander ausgewählt sind aus Alkyl-, Aryl-, alicyclischen und heterocyclischen Resten, und
Z eine kovalente Bindung oder ein Sauerstoffatom darstellt; und
Salzen von N-Nitrosocyclohexylhydroxylamin, N-Phenylglycin und Organoboratsalzen, umfassend ein Anion der Formel



(III)

in der R^1 bis R^4 unabhängig voneinander Alkyl-, Aryl-, Alkaryl-, Aralkyl-, Alkenyl-, Alkinyl-, Silyl-, alicyclische oder gesättigte oder ungesättigte heterocyclische Reste darstellen, einschließlich substituierte Derivate dieser Reste mit der Maßgabe, daß mindestens einer der Reste R^1 bis R^4 ein Alkylrest mit bis zu 8 Kohlenstoffatomen ist; und
neutralen Reduktionsmitteln, die ein oder mehrere labile Wasserstoffatome oder Acylreste aufweisen.

8. Thermisches Bildaufzeichnungselement gemäß Anspruch 7, wobei R^5 H oder eine Phenylgruppe ist, R^6 eine Phenylgruppe ist, R^7 und R^8 niedere Alkylreste sind.

9. Thermisches Bildaufzeichnungselement gemäß Anspruch 7, wobei das neutrale Reduktionsmittel ausgewählt ist aus Thioharnstoffderivaten, Ascorbinsäure, Benzhydrolen, Phenolen, Aminen und Leukofarbstoffen und acylierten Derivaten davon.

10. Thermisches Bildaufzeichnungselement gemäß einem der vorstehenden Ansprüche, wobei mindestens 1 Mol Reduktionsmittel pro Mol Farbstoff anwesend ist.

11. Thermisches Bildaufzeichnungselement gemäß einem der Ansprüche 1 bis 7, umfassend eine der folgenden Kombinationen eines Photokonversionsfarbstoffes und eines Photoreduktionsmittels:

(i) ein Farbstoff der Formel (I) oder Formel (II) wie in Anspruch 5 definiert und ein Reduktionsmittel der Formel (IV) wie in Anspruch 7 definiert;
(ii) ein kationischer Farbstoff und ein Reduktionsmittel der Formel (III) wie in Anspruch 7 definiert; und
(iii) ein Cyanin- oder Quadratsäurefarbstoff und ein acylgeschützter Leukofarbstoff.

12. Thermisches Bildaufzeichnungselement gemäß einem der vorstehenden Ansprüche, wobei das Element ein Farbstoffübertragungssystem, ein Abziehsystem, ein lichtaktivierbares Klebesystem oder ein unimolekulares thermisches Fragmentationssystem ist.

13. Thermisches Bildaufzeichnungselement gemäß Anspruch 12 in Form eines Farbstoffübertragungsdonors, welches Pigmentpartikel in einem Binder dispergiert umfaßt.

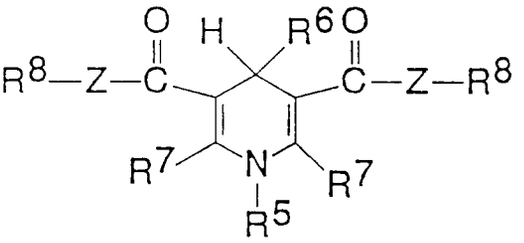
14. Thermisches Bildaufzeichnungselement gemäß Anspruch 13, welches zusätzlich ein Fluorkohlenstoff umfaßt.

15. Bildaufzeichnungsverfahren, umfassend einen Schritt, in dem ein thermisches Bildaufzeichnungselement gemäß einem der vorstehenden Ansprüche Laserbestrahlung bei einer Wellenlänge, die der photothermische Konversionsfarbstoff absorbiert, ausgesetzt wird, wobei die Bedingungen der Aussetzung so gewählt werden, daß die Absorption durch den Farbstoff ausreichend Wärme erzeugt, um ein Bild auf dem hitzeempfindlichen Bildaufzeichnungsmedium zu erzeugen, und das Reduktionsmittel den Farbstoff bleicht.

16. Verfahren gemäß Anspruch 15, wobei das thermische Bildaufzeichnungselement ein Farbstofftransfersystem, ein Abziehsystem, ein lichtaktivierbares Klebesystem oder ein unimolekulares thermisches Fragmentationssystem umfaßt.

17. Verfahren zum Bleichen eines kationischen Farbstoffes, umfassend photobestrahlung des Farbstoffes, wobei der Farbstoff in einen elektronisch angeregten Zustand übergeht, in Gegenwart eines 1,4-Dihydropyridins mit einem

Kern der allgemeinen Formel IV:



(IV)

wobei

R^5 ausgewählt ist aus H, Alkyl-, Aryl-, alicyclischen und heterocyclischen Resten;
R^6 einen Arylrest darstellt; und
R^7 und R^8 unabhängig voneinander ausgewählt sind aus Alkyl-, Aryl-, alicyclischen und heterocyclischen Resten,
und
Z eine kovalente Bindung oder ein Sauerstoffatom darstellt.

Revendications

1. Elément d'imagerie thermique excitable par laser comprenant un colorant de conversion photothermique blanchissable en association à un milieu d'imagerie thermosensible, et un agent photoréducteur pour ledit colorant, ledit agent photoréducteur blanchissant ledit colorant lors d'une excitation par laser de l'élément.

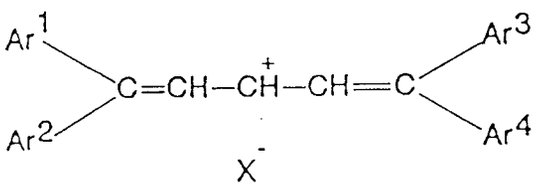
2. Elément d'imagerie thermique selon la revendication 1, dans lequel ledit colorant possède un maximum d'absorption dans la plage de 600 à 1 500 nm.

3. Elément d'imagerie thermique selon la revendication 1 où 2, dans lequel ledit colorant est un colorant cationique ou un colorant neutre.

4. Elément d'imagerie thermique selon la revendication 3, dans lequel ledit colorant est choisi parmi les colorants polyméthine, les colorants pyrylium, les colorants cyanine, les colorants diamines dicationiques, les colorants phénazinium, les colorants phénoxazinium, les colorants acridinium, les colorants xanthène et les colorants squarylium.

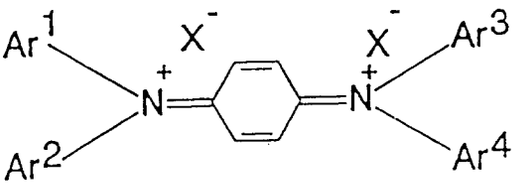
5. Elément d'imagerie thermique selon la revendication 4, dans lequel ledit colorant possède la formule:

(I)



ou

(II)

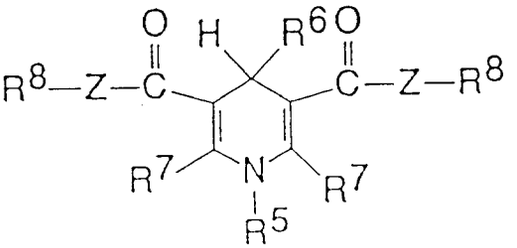


où Ar^1 à Ar^4 représentent indépendamment des groupes aryle de sorte qu'au moins deux de Ar^1 à Ar^4 possèdent un groupe amino tertiaire en position 4 et X est un anion.

6. Elément d'imagerie thermique selon la revendication 5, dans lequel ledit groupe amino tertiaire est choisi parmi les groupes amino dialkyle, les groupes diarylamino ou les substituants cycliques choisis parmi les groupes pyrrolidino, morpholino, pipéridino ou bien fait partie d'un système de cycle condensé et X représente un radical parmi ClO_4, BF_4, CF_3SO_3, PF_6, AsF_6 et SbF_6.

7. Elément d'imagerie thermique selon l'une quelconque des revendications précédentes, dans lequel l'agent réducteur est choisi parmi les composés ayant un noyau de formule:

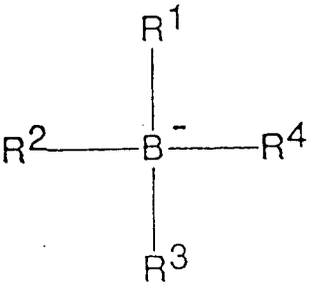
(IV)



dans laquelle:

R^5 est choisi parmi un atome H, un groupe alkyle, aryle, alicyclique ou hétérocyclique;
R^6 représente un groupe aryle;
chaque R^7 et chaque R^8 est choisi indépendamment parmi les groupes alkyle, aryle, alycycliques et hétérocycliques et Z représente une liaison covalente ou un atome d'oxygène; et les sels de la N-nitrosocyclohexylhydroxylamine, la N-phénylglycine et les sels organoborates comprenant un anion de formule:

(III)



dans laquelle R^1 à R^4 représentent indépendamment des groupes alkyle, aryle, alcaryle, aralkyle, alcényle, alcynyle, silyle, alicycliques ou hétérocycliques saturés ou insaturés, y compris les dérivés substitués de ces groupes à condition qu'au moins l'un de R^1 à R^4 soit un groupe alkyle ayant jusqu'à 8 atomes de carbone; et des agents réducteurs neutres possédant un ou plusieurs atomes d'hydrogène labile ou groupes acyle.

8. Elément d'imagerie thermique selon la revendication 7, dans lequel R^5 est un atome H ou un groupe phényle, R^6 est un groupe phényle, R^7 et R^8 sont des groupes alkyle inférieur.

9. Elément d'imagerie thermique selon la revendication 7, dans lequel ledit agent réducteur neutre est choisi parmi les dérivés thiourée, l'acide ascorbique, les benzhydrols, les phénols, les amines et les leuco-colorants et leurs dérivés acylés.

10. Elément d'imagerie thermique selon l'une quelconque des revendications précédentes, dans lequel au moins une mole de l'agent réducteur est présente par mole de colorant.

11. Elément d'imagerie thermique selon l'une quelconque des revendications 1 à 7 comprenant une des combinaisons suivantes de colorants de photoconversion et d'agents photoréducteurs:

(i) un colorant de formule (I) ou de formule (II) tel que défini selon la revendication 5 et un agent réducteur de formule (IV) tel que défini selon la revendication 7;
(ii) un colorant cationique et un agent réducteur de formule (III) tels que définis selon la revendication 7; et
(iii) un colorant cyanine ou squarylium et un leuco-colorant protégé par un groupe acyle.

12. Elément d'imagerie thermique selon l'une quelconque des revendications précédentes, dans lequel ledit élément est un système de transfert de colorant, un système de séparation, un système rendu collant par photons ou un système de fragmentation thermique unimoléculaire.

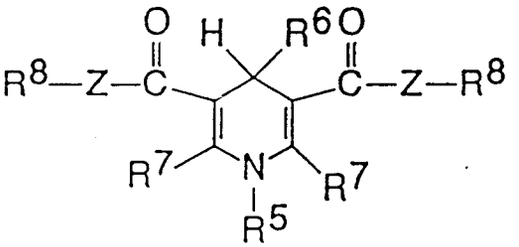
13. Elément d'imagerie thermique selon la revendication 12 sous la forme d'un donneur de transfert de colorant qui comprend des particules de pigment dispersées dans un liant.

14. Elément d'imagerie thermique selon la revendication 13 qui comprend de plus un fluorocarbone.

15. Procédé d'imagerie qui comprend l'étape consistant à exposer un élément d'imagerie thermique selon l'une quelconque des revendications précédentes à une irradiation par laser à une longueur d'onde absorbée par ledit colorant de conversion photothermique, dans des conditions d'exposition telles que l'absorption par ledit colorant engendre suffisamment de chaleur pour former une image dudit milieu d'imagerie thermosensible et ledit agent réducteur blanchit ledit colorant.

16. Procédé selon la revendication 15, dans lequel l'élément d'imagerie thermique comprend un système de transfert de colorant, un système de séparation, un système rendu collant par photons ou un système de fragmentation thermique unimoléculaire.

17. Procédé de blanchiment d'un colorant cationique consistant à irradier par photons ledit colorant en un état électronique excité en présence d'une 1,4-dihydropyridine ayant un noyau de formule générale IV:



dans laquelle:

R^5 est choisi parmi un atome H, les groupes alkyle, aryle, alicycliques et hétérocycliques;
R^6 représente un groupe aryle; et
chaque R^7 et chaque R^8 est choisi indépendamment parmi les groupes alkyle, aryle, alicycliques hétérocycliques, et Z représente une liaison covalente ou un atome d'oxygène.