

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 739 748 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
31.03.1999 Bulletin 1999/13

(51) Int. Cl.⁶: **B41M 5/30**, B41M 5/40

(21) Application number: **96302794.1**

(22) Date of filing: **19.04.1996**

(54) **Laser addressable direct-write media**

Durch Laser direkt beschreibbare Auzeichnungsmaterialien

Moyens de formation d'images en écriture directe par laser

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **20.04.1995 GB 9508028**

(43) Date of publication of application:
30.10.1996 Bulletin 1996/44

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

(72) Inventors:
• **Patel, Ranjan C.**
Little Hallingbury, Essex, CM22 7PP (GB)
• **Van Thien, Tran**
Harlow, Essex (GB)

• **Mott, Andrew W.**
Bishops Stortford, Herts., CM23 2DG (GB)
• **Stibbard, John H.A.**
Harlow, Essex CM20 1NU (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- 0 181 085 **EP-A- 0 331 890**
EP-A- 0 366 461 **EP-A- 0 384 665**
EP-A- 0 599 369 **US-A- 3 404 995**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 739 748 B1

Description

[0001] The invention relates to imaging media addressable by laser irradiation. In particular, the media comprise an IR-absorbing dye and a leuco dye, laser exposure at a wavelength absorbed by the IR dye resulting in conversion of the leuco dye to the corresponding dye.

[0002] There is a substantial interest in laser addressable imaging materials, particularly to produce digitally stored image information in a convenient manner. Materials which do not require further processing following image-forming exposure and which do not generate waste in the imaging process which would require disposal are particularly useful. However, the majority of known laser addressable systems involve physical transfer of a colourant from a donor sheet to a receptor sheet, with the donor sheet then being discarded.

[0003] There are few examples of "direct-write" media, namely single-sheet materials in which an image forms directly as a result of laser exposure, particularly negative-acting materials in which irradiated areas develop image density. Known examples include the thermographic reduction of silver behenate disclosed in EP-A-0582144, EP-A-0599369 and WO95/07822, thermally-stimulated colour-forming reactions between microencapsulated agents described in Japanese publications JP-A-05 124337, JP-A-05 124338, JP-A-05 124339 and JP-A-05 124340, and the thermal decomposition of certain protected leuco dyes disclosed in US-A-4602263, 4720449, 4720450, 4745046, 4818742, 4826976, 4839335, 4904572 and 4960901. In each case, an IR absorbing substance converts incident laser radiation to heat which triggers the image-forming process. There are few restrictions on the identity of the IR absorber so long as it acts as an effective photothermal converter since the image-forming reaction is purely thermal.

[0004] Our British Patent Application No. 9508027.1 describes photochemical interactions between IR dyes and leuco dyes, where the leuco dye acts as a reducing agent leading to bleaching of the IR dye. However, in that application it is desirable that the leuco dyes do not themselves generate colour images on exposure.

[0005] EP-A-0 366 461 discloses an optical recording medium comprising a near infrared absorbent, a basic colorless dye and an organic developer.

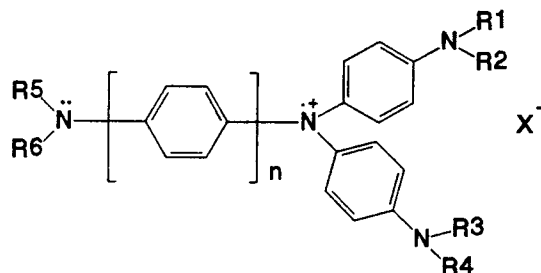
[0006] The present invention provides an alternative direct-write negative acting media based on the photochemical interaction of an IR dye with a leuco dye.

[0007] In accordance with the present invention there is provided a laser-imageable direct-write medium comprising an infrared dye in photoreactive association with a leuco dye, in which irradiation at a wavelength absorbed by said infrared dye converts said leuco dye to the corresponding dye, characterised in that the said infrared dye comprises a chromophore which is formally the product of a one-electron or two-electron oxidation of a p-phenylenediamine or 4,4'-biphenylenediamine.

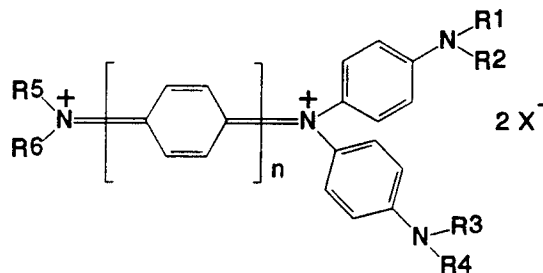
[0008] The media of the present invention have a simple construction and do not require additional oxidising agents or the presence of silver salts (light sensitive or otherwise), although they may optionally be used in combination with thermographic media involving reducible silver salts, as will be described in detail hereinafter. A dye image is produced in direct response to laser irradiation. The image media is capable of high sensitivity and good stability before and after imaging.

[0009] Preferred infrared dyes suitable for use in the invention have a nucleus represented by formula I(a) or I(b):-

I (a)



I (b)



in which n is 1 or 2;

X is an anion derived from a strong acid;

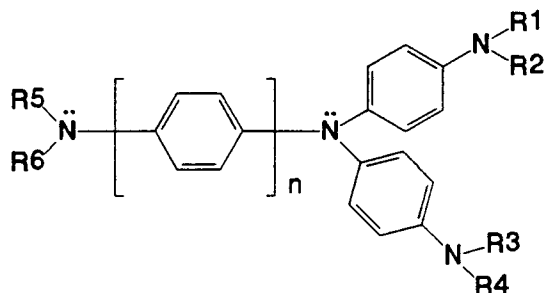
R¹-R⁴ are independently selected from H, alkyl groups (of up to 15 carbons, preferably up to 6 carbons) heterocyclic groups (of up to 10, preferably 6, atoms selected from C,N,O,S), or R¹ together with R² and/or R³ together with R⁴ may complete a cyclic structure of up to 10 (preferably up to 6) skeletal atoms selected from C,N,O,S, or any of R¹-R⁴ or R¹ and R² or R³ and R⁴ may complete a ring fused to the phenyl ring to which the relevant N atom is bonded (e.g. R¹ and R² may complete a julolidine ring system); and

R⁵ and R⁶ independently represent 4-(R⁷R⁸N)-C₆H₄- (where R⁷ and R⁸ have the same definition as R¹-R⁴), alkyl groups (of up to 15 carbons, preferably of up to 5 carbons), aryl groups (of up to 10, preferably 6 carbons), heterocyclic groups (of up to 10, preferably 5 or 6, atoms selected from C,N,O,S), or R⁵ together with R⁶ may complete a cyclic structure of up to 10 (preferably up to 6) skeletal atoms selected from C,N,O,S or R⁵ and/or R⁶ may complete a ring fused to the phenyl ring to which R⁵R⁶N is bonded (e.g., R⁵ and R⁶ may complete a julolidine ring system).

[0010] In the above formula, the rings and substituents R¹-R⁶ may optionally bear one or more additional substituents, such as alkyl groups, aryl groups (including fused aryl rings), hydroxy, alkoxy, thioether, mercapto, nitrile, nitro, halide, ketone, ester, amide and carboxylic acid groups. Preferably n=1 and X is an anion such as ClO₄, CF₃SO₃, BF₄, PF₆, AsF₆.

[0011] Dyes of formula I(a) may be regarded as the products of a one-electron oxidation of the p-phenylenediamines (n=1) or 4,4'-biphenylenediamines (n=2) of formula I(c) (in which n and R¹ - R⁶ have the same meanings as before), while dyes of formula I(b) may be regarded as the products of a two-electron oxidation of the compounds of formula I(c).

I (c)

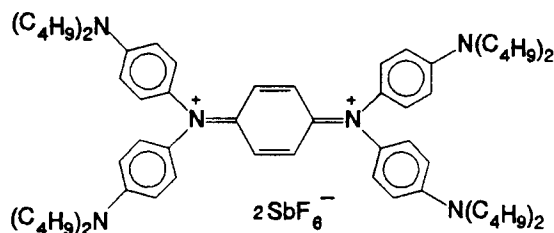


[0012] In compounds of formula I(c), each amino group has associated with it a lone pair of electrons which are in conjugated with the delocalised pi-system of the adjacent aromatic ring. Removal of one electron from the system (i.e., one-electron oxidation) gives compounds which may be represented as the amine cation radicals I(a), and removal of a second electron (two-electron oxidation) gives compounds which may be represented as the quinoneimmonium di-cations I(b). It will be appreciated that each of formulae I(a) and I(b) represents only one of many possible resonance structures, and these formulae must be interpreted as being inclusive of said resonance structures. For example, compounds of formula I(b) could equally well be depicted as bis(amine cation radicals), and compounds of formula I(a) as quinoneimmonium monocations. A further complicating factor is the fact that dyes of formula I(a) may disproportionate to a 1:1 mixture of I(b) and I(c). Thus, for the sake of simplicity, dyes used in the invention will be depicted as quinoneimmonium di-cations as in formula I(b), but this should not be interpreted as excluding monocationic species I(a), nor the presence of significant amounts of the fully-reduced form I(c).

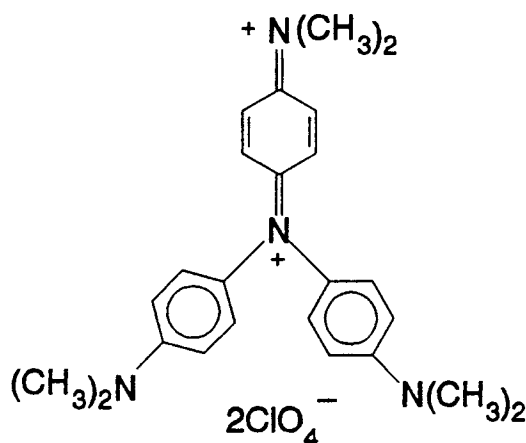
[0013] Infrared dyes of formula I(a) and/or I(b) are disclosed in numerous publications, notably US-A-3404995 US-4656121, WO90/12342, JP63319191 and EP-0599369, and are variously known as diamine dication dyes, amine cation radical dyes, bis(amine cation radical) dyes, immonium dyes, di-immonium dyes etc. Hereinafter, the term "amine cation radical dye" will be used to denote the infrared dyes suitable for use in the invention.

[0014] Examples of amine cation radical dyes of Formula I suitable for use in the invention include:-

(1)



(2)



[0015] Compound (1) is available commercially under the trade name Cyasorb IR 165 from Glendale Protective Technologies Inc.

[0016] Leuco dyes suitable for use in the invention are the essentially colourless reduced forms of visible-absorbing dyes, so that conversion of the leuco to the corresponding dye provides a visible colouration. The leuco dye must be stable to storage at ambient or moderately elevated temperatures in the presence of the IR dye in its ground state. For this reason "protected" leuco dyes, for example, acyl or sulphonyl derivatives are preferred.

[0017] In the presence of the photoexcited IR dye, the leuco dye converts to the corresponding visible dye. It is believed this process involves transfer of an electron from a molecule of the leuco dye to a photoexcited molecule of the IR dye, followed by loss of hydrogen (or the protecting group, if present) to form a molecule of visible dye. The net result is bleaching of the IR dye with concomitant build-up of colour from the visible dye.

[0018] This reaction has been shown to work for IR dyes of the amine cation radical type described above, but not for others. Thus, IR dyes of other types, such as cyanines and squaryliums, undergo bleaching when irradiated in the presence of leuco dyes but do not convert the leuco dyes to the corresponding visible dyes to an appreciable extent. This suggests that initial electron transfer takes place as described above, but thereafter the conditions do not favour the loss of hydrogen or the protecting group. Why the situation should be different in the case of the amine cation radical dyes is not clear, although the presence of a double positive charge in the chromophore may be significant. It is also noteworthy that dyes such as (1) and (2) can undergo one-electron reduction to form species that are themselves IR-absorbing. Hence two-photon processes may be involved. In any event, the fact that the choice of IR dye is critical provides evidence of the photochemical nature of the process. If it were purely thermal (as is the case in direct-write media of the prior art), then any substance capable of absorbing IR radiation and converting it to heat would be effective.

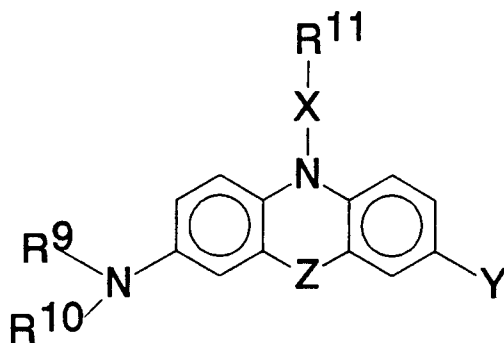
[0019] Leuco dyes suitable for use in the invention are capable of transferring an electron to a photoexcited dye. This indicates that the HOMO (highest occupied molecular orbital) of the leuco dye has a higher energy than the LUMO (lowest unoccupied molecular orbital) of the photoexcited IR dye. The relationship between the energy of these orbitals is illustrated in Figure 1 of the accompanying drawings. In Figure 1, A represents the relevant orbitals of the IR dye in its ground state with the HOMO at energy E and the LUMO at higher energy E*. On photoexcitation, an electron is promoted to the higher energy orbital leaving a vacancy in the lower energy orbital at energy E, which may now be described as the LUMO of the photoexcited dye. This is represented by B in the figure. A number of possibilities for the energy of the HOMO of the leuco dye (E_{leuco}) are represented by C. If this E_{leuco} is higher than the energy level E of the LUMO of the photoexcited dye (B), an electron is transferred from the HOMO of the leuco to the LUMO of the photoexcited dye.

[0020] The ideal situation occurs when the IR dye and leuco dye are selected so that $E < E_{\text{leuco}} < E^*$ so that electron transfer from the leuco dye to the IR dye tends to occur when the IR dye is in its photoexcited state. If the energy level of the HOMO of the leuco dye is too high, i.e., E_{leuco} is greater than E^* , electron transfer will tend to occur in the absence of photoexcitation, being energetically favourable. This leads to spontaneous bleaching of the IR dye on mixing of the IR dye with the leuco dye. This situation may be alleviated to a certain extent by coating the IR dye and the leuco dye in separate layers and/or using sterically hindered leuco dyes to inhibit the ground state reaction.

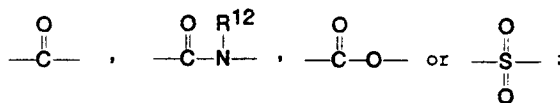
[0021] The relevant energy levels may be estimated by techniques familiar to those skilled in the art, such as molec-

ular modelling using appropriate computer software e.g., CAChe, available from Tectronix, or measurements of oxidation potential. Alternatively or additionally, candidate combinations of IR dye and leuco dye may be screened empirically by coating roughly equimolar amounts of each on a suitable substrate (in the same or adjacent layers, with or without added binder) and monitoring the absorption spectrum before and after irradiation at or near the absorption maximum of the IR dye. Prior to irradiation, there should be a stable, intense IR absorption, with little or no build up of visible colour. Subsequent to irradiation, there should be an immediate visible colouration.

[0022] A preferred class of leuco dye, suitable for use with dyes such as compound (1), are N-acyl or N-sulphonyl derivatives of leuco-phenazine, -phenoxazine and -phenothiazine dyes. These have a nucleus of formula



in which X represents



Y represents H, NR^9R^{10} , alkoxy, alkylthio, aryloxy, arylthio, alkyl, aryl or halogen;

Z represents O, S, or NR^{13} ;

R^{12} represents H, alkyl or aryl;

R^9 , R^{10} and R^{13} are independently selected from H, alkyl, aryl, alkylcarbonyl, arylcarbonyl, alkylsulphonyl or arylsulphonyl, or

R^9 and R^{10} represents the atoms necessary to complete a cyclic structure fused to the nucleus having skeletal atoms selected from C, N, O and S; and R^{11} represents any group which will not prevent oxidative cleavage of the X-N bond.

[0023] In the above definitions, alkyl, alkoxy and alkylthio groups contain up to 15, preferably up to 5, carbon atoms; and aryl, aryloxy and arylthio groups contain up to 10, preferably up to 6, carbon atoms. In the above formula, the rings and substituents may optionally bear one or more additional substituents, such as alkyl groups, aryl groups including fused aryl rings, hydroxy, alkoxy, thioether, mercapto, nitrile, nitro, halide, ketone, ester, amide and carboxylic acid groups.

[0024] In preferred structures in accordance with Formula II, X represents a carbonyl group and R^{11} represents an alkyl or aryl group, most preferably aryl, such as phenyl or alkoxyphenyl. R^{11} may represent a polyvalent residue linking together two or more leuco-azine structures. Also in preferred structures, R^9 and R^{10} represent alkyl groups, Y represents NR^9R^{10} , and Z represents O, or NR^{13} where R^{13} is alkyl or aryl.

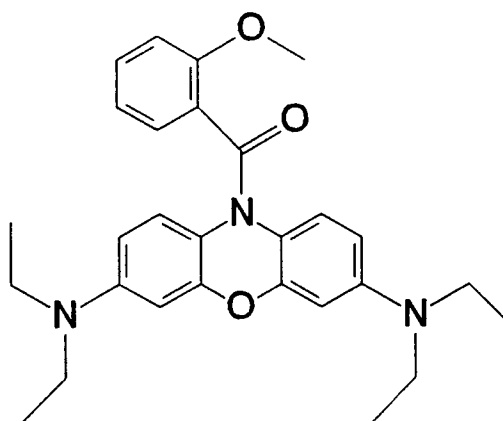
[0025] Leuco dyes of Formula II have been disclosed in connection with thermographic media employing nitrate salts as oxidising agents in US-A-4563415, and in photothermographic media of the "dry silver" type employing silver salts as oxidising agents in US-A-4594307 and EP-A-0671393 and EP-A-0681210.

[0026] Examples of leuco dyes in accordance with Formula II include the following (with the colour of the corresponding dye indicated in brackets):-

5

10

15



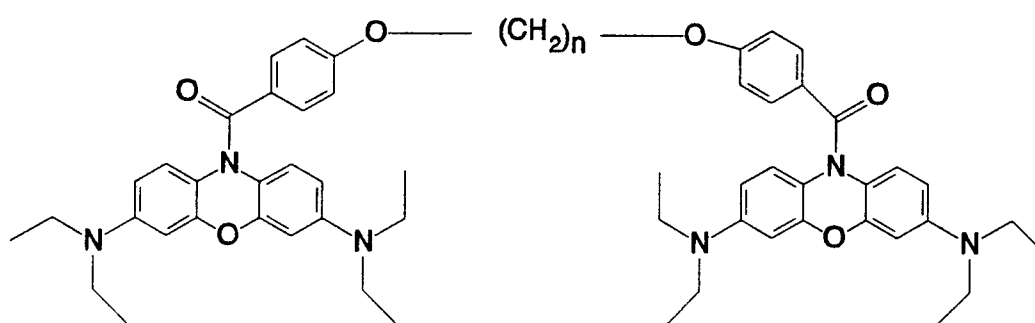
20

L1 (cyan)

25

30

35



40

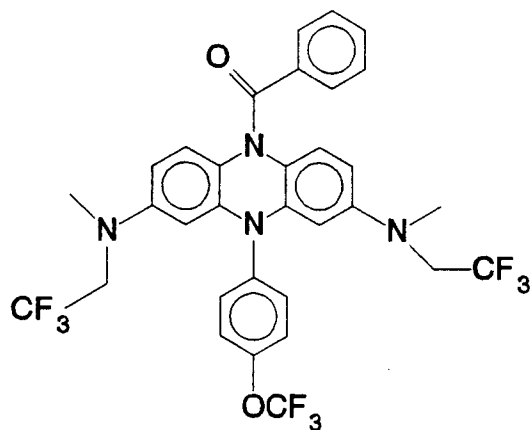
n=5 L2 (cyan)

n=10 L3 (cyan)

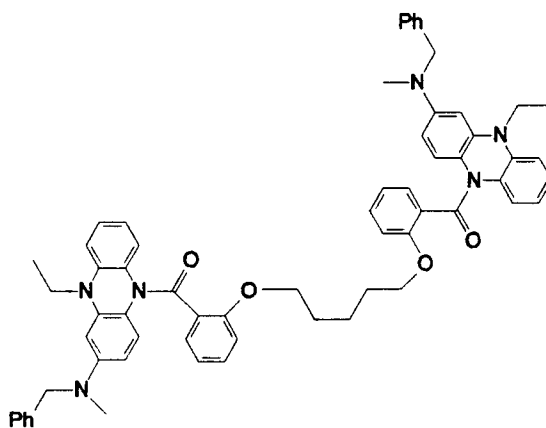
45

50

55



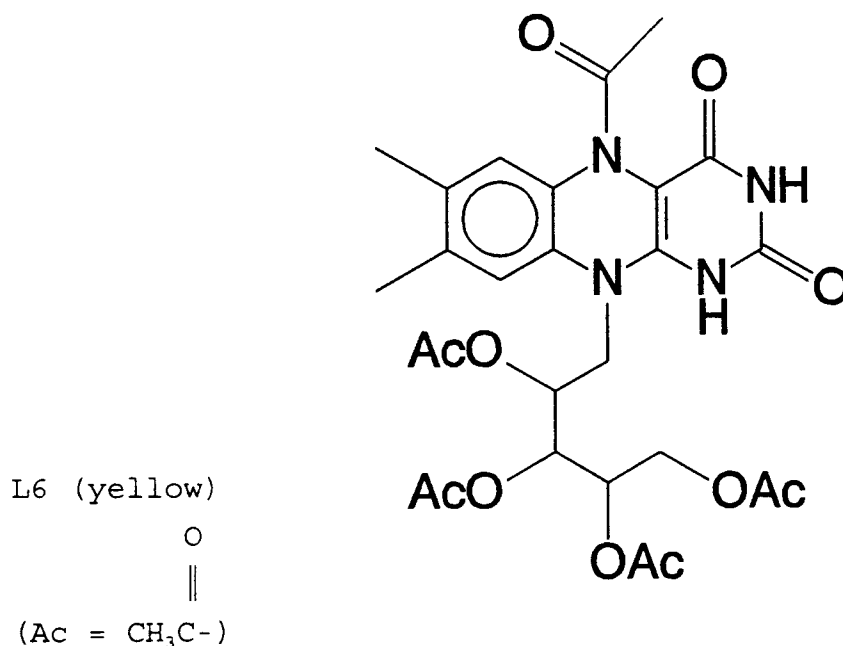
L4 (magenta)



L5 (magenta)

[0027] Leuco dyes of Formula II may be prepared by reduction of the corresponding azine dyes, for example, with sodium hydrosulphide and in situ reaction with a compound of formula $R^{11}-X-Cl$, where R^{11} and X have the same meanings as before, as described, for example, in US-A-4563415 and references therein.

[0028] Formula II does not include all the leuco dyes suitable for use in the invention. Others include:-



[0029] Compound L6 may be prepared from riboflavin by reduction with Zn/acetic acid followed immediately by acylation with acetyl chloride.

[0030] Direct write imaging elements in accordance with the invention comprise a substrate bearing, in one or more coated layers, the amine cation radical IR dye as described above in photoreactive association with one or more leuco dyes. The substrate may be any suitable dimensionally-stable material, such as paper or plastic film. A preferred material is polyester film of about 50-200 microns, particularly of about 100 micron thickness.

[0031] "Photoreactive association" means that the IR dye and the leuco dye must be capable of reacting with each other during laser irradiation of the former. This is clearly possible if both are coated in the same layer, and is also possible when they are coated in separate layers, provided the separate layers melt or otherwise permit mixing of the reagents at the elevated temperatures generated by laser irradiation. As indicated previously, coating the ingredients in separate layers can inhibit unwanted ground state reactions. The ingredients may be coated with or without binders, suitable binders including polyvinylbutyral, vinyl resins, cellulose esters and the like. In a preferred construction, the leuco dye is coated as an underlayer in a binder comprising a vinyl resin such as a copolymer of vinyl chloride and vinyl acetate for example, of the type supplied by Union Carbide under the trade name "VYNS", while the IR dye is coated as an upper layer in a binder comprising polyvinylbutyral for example, of the type supplied by Monsanto under the trade name "Butvar".

[0032] A protective topcoat may be added, which may be any transparent material capable of being coated without disturbing the IR dye/leuco dye layer(s). Since the latter are normally coated from organic solvents such as acetone, MEK and the like, preferred topcoats are water soluble polymers such as polyvinylalcohol or gelatin.

[0033] The IR dye is generally present in an amount sufficient to provide an optical density of at least 0.5 at the intended imaging wavelength, a thin layer containing a high loading of dye being preferable to a thicker layer with a lower loading of dye. The leuco dye is generally present in an amount corresponding to at least one molar equivalent of the IR dye, preferably to at least two molar equivalents, most preferably three molar equivalents. It is a surprising feature of the invention that one molecule of IR dye can apparently convert two or more molecules of leuco dyes to the corresponding dye when the conversion is, as previously theoretically demonstrated not purely thermal. Depending on the desired colour of the generated image, two or more different leuco dyes may be combined in the same coating, for example, to give a black image.

[0034] Nitrate salts may be incorporated in the media, especially when the leuco dye is of the type depicted in Formula II. A preferred nitrate salt is nickel nitrate, although any of the nitrate salts disclosed in US-A-4563415 may be used. The effect of adding a nitrate salt is to facilitate thermal oxidation of the leuco dye to the corresponding dye, in addition to the photochemical oxidation mediated by the IR dye. Hence there is an increase in overall imaging speed, although this may be accompanied by a decrease in shelf stability due to the increased thermal sensitivity. Thus, there may be a per-

ceptible increase in Dmin on prolonged storage before or after imaging. If used, the nitrate salt is preferably coated in the same layer as the leuco dye, in an amount corresponding to roughly 50% by weight of the leuco dye.

[0035] Any of the well known coating techniques may be used, such as knife coating, slot coating, roller coating, bar coating or spin coating.

5 **[0036]** Materials in accordance with the invention are imaged by exposure to laser radiation. Any laser emitting in the near IR may be used, but diode lasers and YAG lasers are particularly suitable. In exposed areas, the absorption due to the IR dye disappears, to be replaced by a shorter wavelength absorption corresponding to the oxidised form of the leuco dye(s) originally present in the coating. No thermal or other type of processing is necessary. Furthermore, the density of the image produced is directly proportional to the intensity of the laser exposure, and so continuous tone
10 imaging is possible. Hence the materials are particularly useful in medical imaging applications, for example to record the output of digital X-ray equipment, magnetic resonance scanners, CAT scanners and ultrasound scanners.

[0037] Best results are obtained from a relatively high intensity laser exposure, for example, of at least 10^{17} photons/cm²/sec. For a laser diode emitting at 830 nm, this corresponds approximately to an output of 0.1W focused to a 20 micron spot. In the case of YAG laser exposure at 1064nm, a flux of at least 3×10^{18} photons/cm²/sec is preferred,
15 corresponding roughly to an output of 2W focused to a 20 micron spot.

[0038] Any of the known scanning devices may be used, such as flat-bed scanners, external drum scanners or internal drum scanners. In these devices, the material to be imaged is secured to the drum or bed for example, by vacuum hold-down and the laser beam is focused to a spot of about 20 microns diameter on the IR-absorbing layer. This spot is scanned over the entire area to be imaged while the laser output is modulated in accordance with electronically
20 stored image information. Two or more lasers may scan different areas of the coating 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 coated side, but alternatively may be through the substrate if the latter is transparent to the laser radiation.

[0039] In a further embodiment of the invention, the imaging media of the invention may be used in combination with thermographic media comprising a silver salt and a developer capable of reducing said silver salt. Thermographic media based on the reduction to silver metal of light-insensitive silver salts (such as silver salts of fatty acids) by reducing agents (such as gallate esters, hindered phenols etc.) are well known, and provide a black image on a colourless background in response to heat. EP0582144, EP0599369 and WO95/07822 disclose the incorporation of infrared-absorbing dyes in such media, enabling address by a scanning laser, absorption of the laser radiation by the IR dye
30 generating sufficient heat to trigger the redox reaction between the developer and silver salt. Amine cation radical dyes (as used in the present invention) are among the IR dyes disclosed as suitable for this purpose. The media disclosed EP0582144, EP0599369 and WO95/07822 are of the direct-write type in that image density is generated directly by laser exposure, but it is also possible to amplify the directly-formed image by a uniform, post-exposure heat treatment, as disclosed in European Patent Application No. 94115226.6, filed September 27 1994. A problem associated with
35 media of this type is the colour (tone) of the silver image formed. Ideally, this should be a neutral black, but in practice is frequently found to be brown, even when toning agents such as phthalazine or phthalazinone are present. When an amine cation radical dye is used as the IR absorber, the problem may be solved by additionally incorporating in the media leuco dye capable of photoreducing said amine cation radical dye with concomitant generation of a visible dye, in accordance with the invention described hereinbefore. The colouration provided by the photogenerated dye aug-
40 ments the thermographic silver image and serves to modify its tone. Thus, cyan-forming leuco dyes are particularly preferred in this embodiment of the invention, as they can convert a yellowish-brown image tone to a pleasing blue-black. Imaging elements in accordance with this aspect of the invention typically comprise a substrate bearing, in one or more coated layers, a laser-imageable direct-write medium as defined previously, which medium additionally comprising a binder, a silver salt and a developer which is a reducing agent for said silver salt.

45 **[0040]** The substrate may be any suitable dimensionally-stable material, as described previously, but is preferably a polyester film with a thickness of about 50 to 100µm. The binder, silver salt and developer may be selected from the relevant materials disclosed in the prior art e.g., as disclosed in EP0582144, EP0599369 and WO95/07822 (which are hereby incorporated by reference). Preferred binders are polyvinylbutyral, vinyl resins, acrylic resins, cellulose esters and the like. Preferred silver salts are light-insensitive silver salts of organic acids, notably silver behenate. Preferred
50 developers are hindered phenols or alkyl esters of hydroxybenzoic acids such as methyl gallate, propyl gallate etc. Other ingredients may also be present, such as toners, surfactants, coating aids etc. as described in the prior art. The relative proportions of the various ingredients are also as described in the prior art.

[0041] All the ingredients may be contained within a single coated layer, or may be distributed over two or more layers. The leuco dye and amine cation radical dye constituting the direct-write media of the invention may be coated separately from the thermographic silver salt media (e.g., as a topcoat), or may be added to the layer(s) comprising the thermographic media. A preferred construction comprises (in sequence) a transparent polyester film substrate, a first layer comprising silver behenate, developer and leuco dye dispersed in a binder, and a second layer comprising IR-absorbing amine cation radical dye in binder. A protective topcoat (e.g., of gelatin, polyvinylalcohol etc.) may be added, but is not

essential.

[0042] Imaging may be carried out using the methods and apparatus detailed earlier. Optionally, the imaged element may be subjected to uniform thermal processing (e.g., at about 70 to 130°C for about 5 to 30 seconds) to intensify the silver image.

[0043] The invention is hereinafter described by way of example only with reference to Figure 2 which shows the changes in density occurring in the IR and 670 nm region on laser address when addressed off-peak (830 nm) and on-peak (987 nm).

EXAMPLES

[0044] In the following examples, IR165 refers to "Cyasorb IR165" which is a bis(amine cation radical) dye as shown in structure (1) above, and was obtained from Glendale Protective Technologies Inc.

[0045] Leuco dyes L1-L6 had the structure shown above, and were prepared from the corresponding dyes by reduction followed by acylation in situ, according to known methods as disclosed in US-A-4563415, and British patent application nos. 9404805.5 and 9404806.3.

Example 1

[0046] This example compares the ability of various IR dyes to oxidise leuco-phenoxazines to the corresponding dyes as a result of laser irradiation.

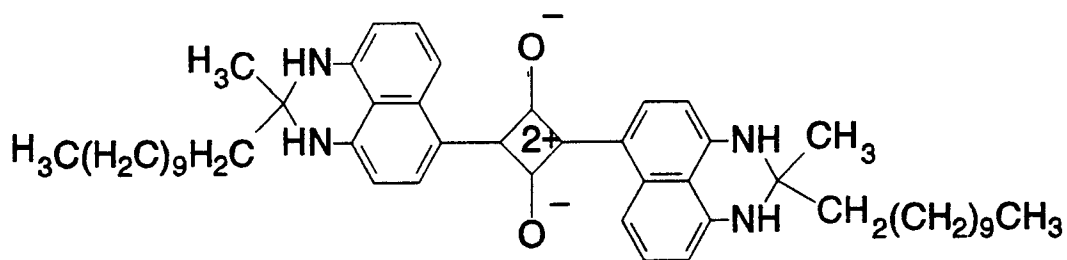
[0047] The following formulations were coated on unsubbed 100 micron polyester base at 12 micron wet thickness using a wire wound bar, and air dried:-

	Element 1	Element 2(c)	Element 3(c)
2-butanone	4.0g	4.0g	4.0g
ethanol	0.4g	0.3g	0.4g
IR165	0.2g	-	-
Dye A	-	0.08g	-
Dye B	-	-	0.1g
L2	0.01g	-	-
L3	-	0.05g	0.1g

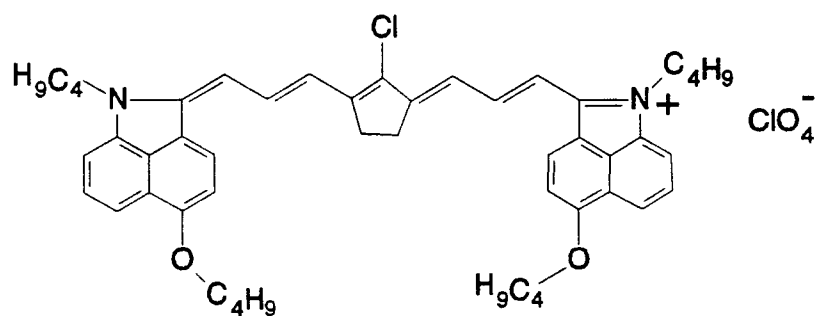
(c) = control

Each coated element had an optical density (OD) at 830nm in the range 1.0-1.8.

Dye A and Dye B had the following structures:-



Dye A



Dye B

[0048] Samples of each coating were mounted on an external drum scanner and imaged with a laser diode delivering 110 mw at 830nm, focused to a 20 micron spot, then examined spectrophotometrically. The following table records the observed changes in OD, both in the IR and at 670nm, that resulted from line scans at 200 cm/sec:-

Element	Change in OD	
	IR	670nm
1	-1.3	+1.0
2(c)	-1.2	<0.1
3(c)	-0.8	<0.1

(c) = control

[0049] The results show that all three coatings suffered extensive bleaching in the IR, but only Element 1 showed significant conversion of the leuco dye to the corresponding dye. These results are not consistent with a simple thermographic mechanism.

Example 2

[0050] This example demonstrates the use of a variety of leuco dyes in the invention.

[0051] Two-layer constructions were prepared by coating unsubbed polyester base with an underlayer comprising a binder and leuco dye, air drying, then applying a topcoat of IR165 in a binder. Both coatings were made by wire-wound bar at 12 microns wet thickness. The layer compositions were as follows:-

Underlayer - leuco dye (0.2g), VYNS (0.1G), 2-butanone (4.4g).

Toplayer - IR165 (0.2g), Butvar B-76 (0.1g), ethanol (0.4g), 2-butanone (4.0g)

[VYNS is a vinyl resin supplied by Union Carbide, and Butvar B-76 is a polyvinylbutyral supplied by Monsanto]

[0052] Samples were imaged as described in Example 1, and the following table records the identity of the leuco dyes tested, the colour produced in imaged areas, and the optical density generated by line scans at 200cms/sec:-

Element	Leuco	Dye Colour	OD
4	L1	cyan	2.4
5	L4	magenta	1.45
6	L5	magenta	0.55
7	L6	yellow	0.6

Example 3

[0053] This example shows the effect of varying the ratio of IR dye to leuco dye. A first series of coatings were made, similar to Element 4 of Example 2 except that the quantity of IR165 in the top layer was varied from 0.01g to 0.20g.

[0054] A second series was also prepared, identical to the first except that the underlayer additionally comprised 0.1g nickel nitrate.

[0055] Imaging was carried out as described previously, and the following table records the molar percentage of IR dye (relative to the leuco) and the corresponding OD generated at 670nm:-

IR DYE (mol%)	OD(670nm)	OD(670nm)(with NiNO ₃)
2	0.1	nd
4	0.1	0.55
8	0.8	0.95
17	1.2	2.35
25	2.3	2.45
33	2.3	nd

nd = not determined

[0056] Sensitivity is seen to increase with increasing amounts of IR dye until the molar ratio of IR dye to leuco dye reaches approximately 1:3, at which point it levels off.

[0057] There is also a clear increase in sensitivity when nickel nitrate is present.

Example 4

[0058] This example demonstrates the continuous tone properties of media in accordance with the invention.

[0059] Samples of Element 4 of Example 2 were imaged as described previously at a number of different scan rates in the range 200 - 1000 cm/sec. The absorption spectrum of the exposed coatings were recorded in each case, and

Fig. 2(a) shows the results. As the scan rate decreased (i.e. energy input increased), there was a progressive build-up of dye density at 670nm and a corresponding bleaching of the IR dye absorption band.

[0060] The experiment was repeated using a different laser diode delivering 167mW at 987nm which was more closely matched to the absorption maximum of IR165. The results are shown in Fig. 2(b). For a given scan rate, the build-up of cyan density is greater for exposure at 987 rather than 830nm. Surprisingly, the bleaching of the IR absorption is less efficient, but this does not affect the usefulness of the invention.

Example 5

[0061] A further sample of Element 4 was imaged via the 830nm laser diode with the laser power modulated during scans between 1mW and 116mW in 256 steps in accordance with image information at 1200 dpi in order to simulate continuous tone exposure. The scan speed was 150 cm/sec. This produced a blue-green image of excellent tonal gradation and resolution, with Dmax of 2.4.

[0062] The process was repeated using Element 8, which was prepared in identical fashion to Element 4 - 7 except that instead of a single leuco dye, the underlayer comprised 0.1g each of L1 and L5. In this case a dark blue-grey image was obtained, with Dmax 1.2.

Example 6

[0063] This Example demonstrates the combination of direct-write media in accordance with the invention with silver behenate thermographic media.

[0064] The following formulation was coated on unsubbed polyester base at 36μm wet thickness using a wire-wound bar:

binder solution	4.5g
silver behenate (10%w/w dispersion in 2-butanone)	3.0g
phthalazinone	0.05g
leuco dye L1	0.15g
methyl gallate	0.075g

[0065] After air drying, the following solution was applied as a topcoat at 12μm wet thickness using a wire-wound bar:

binder solution	0.5g
IR165	0.2g
2-butanone	5.5g

[0066] For both layers, "binder solution" refers to a 20%w/w solution in 2-butanone of poly(tetrahydrophyranyl methacrylate), prepared as described in WO92/09934.

[0067] Imaging was carried out as described in Example 4 using the 987 nm laser diode source, and the imaged element placed in an oven at 85°C for 20 seconds. A dense blue-black image was obtained for scan speeds of 600 cm/sec or less.

[0068] A similar element was prepared without the leuco dye, and was subjected to the same imaging and processing routine. Although a silver image of similar density was obtained, it was noticeably browner in appearance.

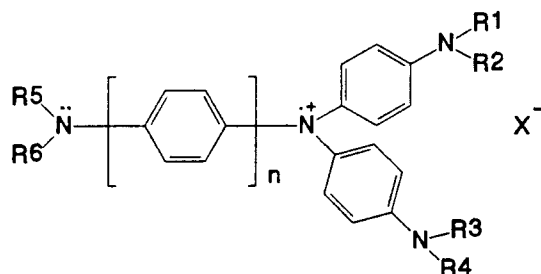
Claims

1. A laser-imageable direct write medium comprising an infrared dye in photoreactive association with a leuco dye, in which irradiation of the medium at a wavelength absorbed by said infrared dye converts said leuco dye to the cor-

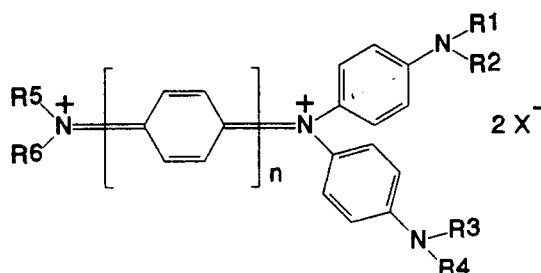
responding dye, characterised in that the said infrared dye comprises a chromophore which is formally the product of a one-electron or two-electron oxidation of a p-phenylenediamine or a 4,4'-biphenylenediamine.

2. A laser-imageable direct write medium according to Claim 1 wherein said infrared dye has a nucleus of formula I(a) or I(b) below:-

I (a)



I (b)



in which $n = 1$ or 2 ,

wherein

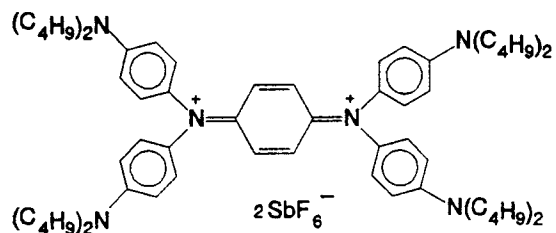
X is an anion derived from a strong acid;

R^1 - R^4 are independently selected from H, alkyl groups of up to 15 carbons, heterocyclic groups of up to 10 atoms selected from C,N,O,S, or R^1 together with R^2 and/or R^3 together with R^4 may complete a cyclic structure of up to 10 skeletal atoms selected from C,N,O,S, or any of R^1 - R^4 or R^1 and R^2 or R^3 and R^4 may complete a ring fused to the phenyl ring to which the relevant N atom is bonded; and

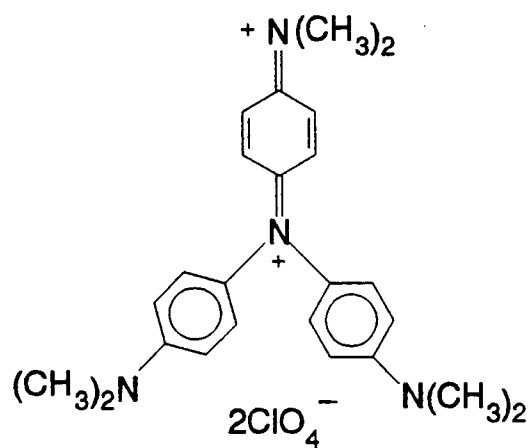
R^5 and R^6 independently represent 4-(R^7R^8N)- C_6H_4 - (where R^7 and R^8 have the same definition as R^1 - R^4), alkyl groups of up to 15 carbons, aryl groups of up to 10 carbons, heterocyclic groups of up to 10 atoms selected from C,N,O,S, or R^5 together with R^6 may complete a cyclic structure of up to 10 skeletal atoms selected from C,N,O,S or R^5 and/or R^6 may complete a ring fused to the phenyl ring to which R^5R^6N is bonded.

3. A laser-imageable direct write medium according to Claim 2 wherein said infrared dye is selected from:-

(1)

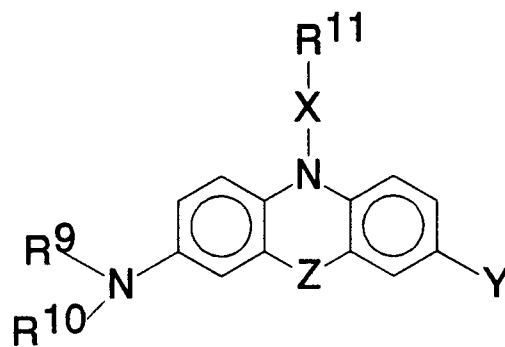


(2)



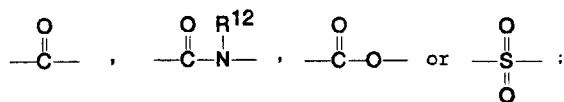
4. A laser-imageable direct write medium according to any preceding claim, wherein said leuco dye is a protected leuco dye, preferably an acyl or sulphonyl derivative.
5. A laser-imageable direct write medium according to Claim 4 wherein said leuco dye has a nucleus of formula II:

II



wherein

X represents



Y represents H, NR^9R^{10} , alkoxy, alkylthio, aryloxy, arylthio, alkyl, aryl or halogen;

Z represents O, S, or NR^{13} ;

R^{12} represents H, alkyl or aryl;

R^9 , R^{10} and R^{13} are independently selected from H, alkyl, aryl, alkylcarbonyl, arylcarbonyl, alkylsulphonyl or arylsulphonyl, or

R^9 and R^{10} represents the atoms necessary to complete a cyclic structure fused to the nucleus having skeletal atoms selected from C, N, O and S; and R^{11} represents any group which will not prevent oxidative cleavage of the X-N bond.

6. A laser-imageable direct write medium according to Claim 5 wherein:

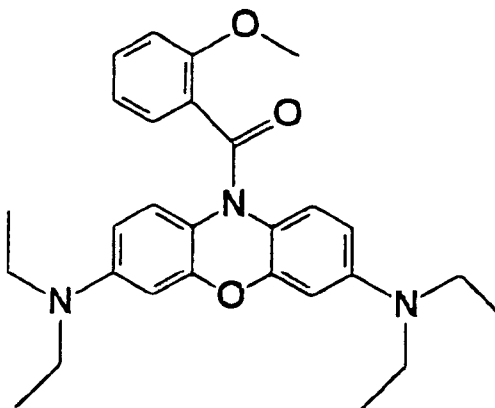
X is a carbonyl group

R^{11} is an alkyl or aryl group.

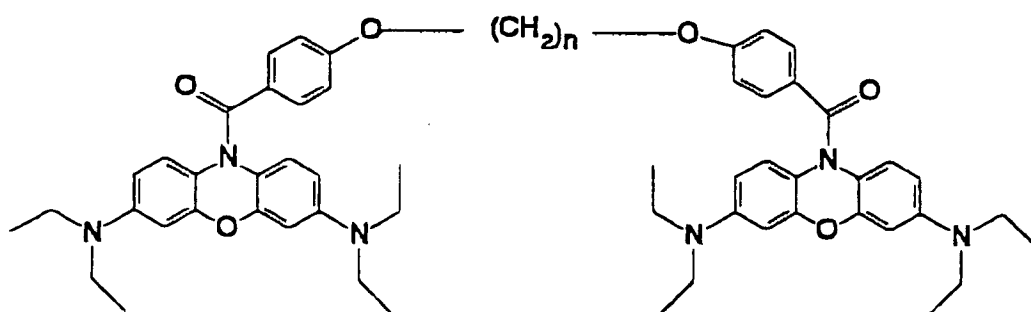
R^9 and R^{10} represent alkyl groups

Y represents NR^9R^{10} , and Z represents O or NR^{13} where R^{13} is alkyl or aryl.

7. A laser imageable direct write medium according to Claim 5 wherein said leuco dye is selected from

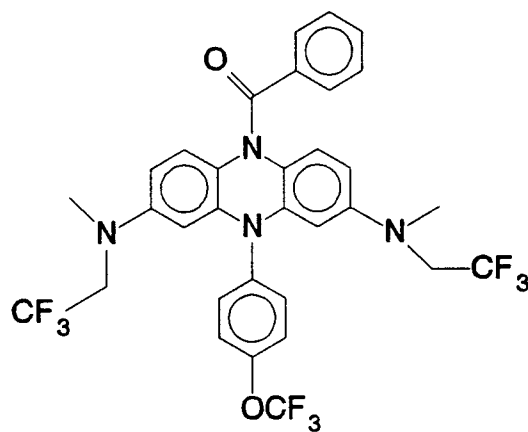


L1 (cyan)

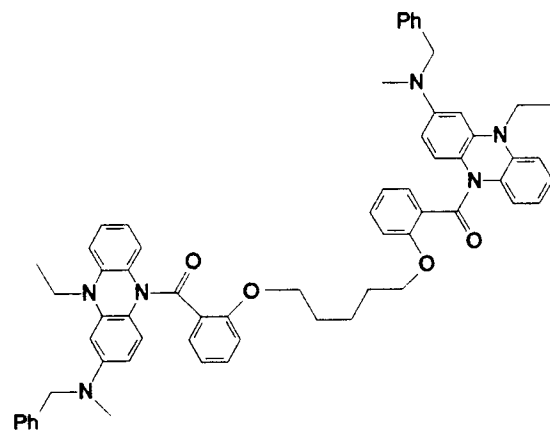


n=5 L2 (cyan)

n=10 L3 (cyan)

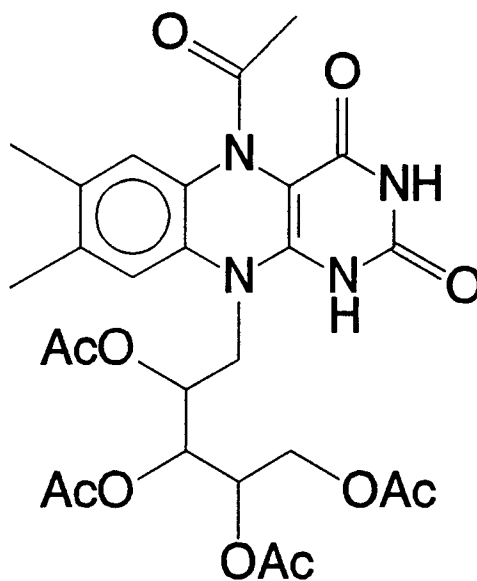


L4 (magenta)

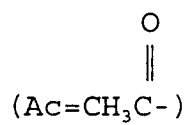


L5 (magenta)

8. A laser-imageable direct write medium according to Claim 1 wherein said leuco dye is:



L6 (yellow)



9. A laser-imageable direct write medium according to any preceding claim wherein either:

said IR dye and said leuco dye are present in the same layer on a substrate or
said IR dye and said leuco dye are coated in separate layers on a substrate.

10. A laser-imageable direct write medium according to Claim 9 wherein said dye layer(s) additionally comprise a binder selected from polyvinylbutyral, vinyl resins and cellulose esters.

11. A laser-imageable direct write medium according to any preceding claim wherein said leuco dye is present in an amount corresponding to at least one preferably at least three, molar equivalent of the IR dye.

12. A laser-imageable direct write medium according to any preceding claim additionally comprising a silver salt and a developer capable of reducing said silver salt.

13. A laser-imageable direct write medium according to Claim 12 wherein said silver salt is silver behenate and said developer is hindered phenol or alkyl ester of hydroxybenzoic acids.

14. A method of imaging a photographic medium comprises exposing a laser-imageable direct-write medium according to any preceding claim to laser irradiation.

15. A method of imaging a photographic medium according to Claim 14 wherein said laser irradiation has an intensity of at least 10^{17} photons/cm²/sec.

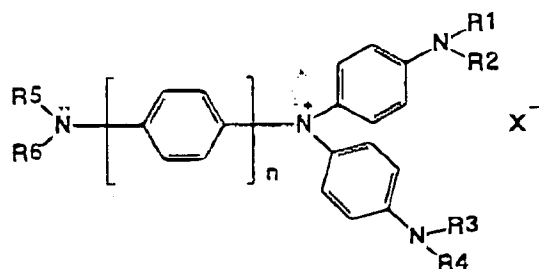
Patentansprüche

1. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium, umfassend ein Infrarotfarbstoff in photoreaktiver Verbindung mit einem Leukofarbstoff, wobei Bestrahlung des

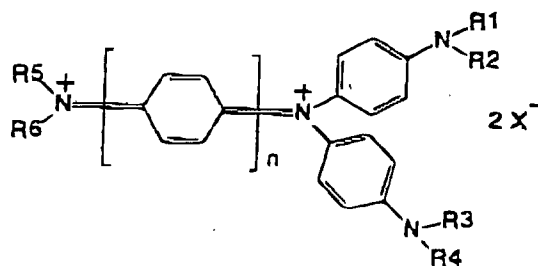
Mediums bei einer Wellenlänge die vom Infrarotfarbstoff absorbiert wird, den Leukofarbstoff in den entsprechenden Farbstoff umwandelt, dadurch gekennzeichnet, daß der Infrarotfarbstoff ein Chromophor umfaßt, das formal das Produkt einer Einelektronen- oder Zweielektronenoxidation eines p-Phenylendiamins oder 4,4'-Biphenylendiamins ist.

2. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 1, wobei der Infrarotfarbstoff einen Kern der nachstehenden Formeln I (a) oder I (b) aufweist:

1 (a)



I (b)



wobei

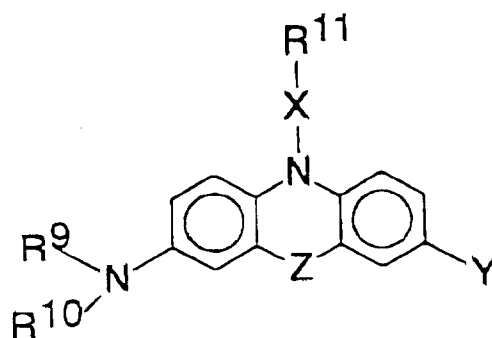
n 1 oder 2 ist;

X ein Anion einer starken Säure ist;

R¹-R⁴ unabhängig voneinander aus H, Alkylresten mit bis zu 15 Kohlenstoffatomen, heterozyklischen Resten mit bis zu 10 Atomen, ausgewählt aus C, N, O, S ausgewählt sind, oder R¹ zusammen mit R² und/oder R³ zusammen mit R⁴ eine zyklische Struktur mit bis zu 10 Ringatomen, ausgewählt aus C, N, O, S vervollständigen können oder irgendwelche der Reste R¹-R⁴ oder R¹ und R² oder R³ und R⁴ einen, an den Phenylring, an den das maßgebliche Stickstoffatom gebunden ist, kondensierten Ring vervollständigen können, und R⁵ und R⁶ unabhängig voneinander 4-(R⁷R⁸N)-C₆H₄- (wobei R⁷ und R⁸ wie R¹-R⁴ definiert sind), Alkylreste mit bis zu 15 Kohlenstoffatomen, Arylreste mit bis zu 10 Kohlenstoffatomen, heterozyklische Reste mit bis zu 10 Atomen, ausgewählt aus C, N, O, S darstellen, oder R⁵ zusammen mit R⁶ eine zyklische Struktur mit bis zu 10 Ringatomen, ausgewählt aus C, N, O, S, vervollständigen können, oder R⁵ und/oder R⁶ einen, an den Phenylring, an den R⁵R⁶N gebunden ist kondensierten Ring vervollständigen können.

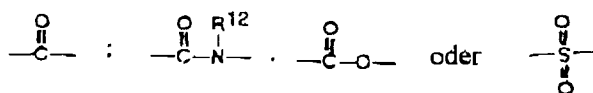
3. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 2, wobei der Infrarotfarbstoff ausgewählt ist aus:

II



wobei

X



ist

Y H, NR⁹R¹⁰, Alkoxy, Alkylthio, Aryloxy, Arylthio, Alkyl, Aryl oder Halogen bedeutet;

Z O, S oder NR¹³ ist;

R¹² H, Alkyl oder Aryl ist;

R⁹, R¹⁰ und R¹³ unabhängig voneinander aus H, Alkyl Aryl Alkylcarbonyl, Arylcarbonyl, Alkylsulphonyl, Arylsulphonyl ausgewählt sind oder R⁹ und R¹⁰ die Atome bedeuten, die notwendig sind, um eine an den Kern kondensierte zyklische Struktur zu vervollständigen, die Skelettatome hat, die aus C, N, O und S ausgewählt sind und R¹¹ eine Gruppe, die die oxidative Spaltung der X-N Bindung nicht verhindert, darstellt.

6. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 5, wobei:

X eine Carbonylgruppe,

R¹¹ ein Alkyl- oder Arylrest,

R⁹ und R¹⁰ Alkylreste

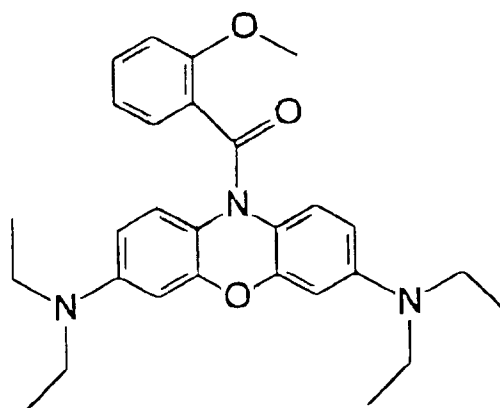
Y NR⁹R¹⁰ und Z O oder NR¹³ bedeutet, wobei R¹³ ein Alkyl- oder Arylrest ist.

7. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 5, wobei der Leukofarbstoff ausgewählt ist aus:

5

10

15



L1 (cyan)

20

25

30

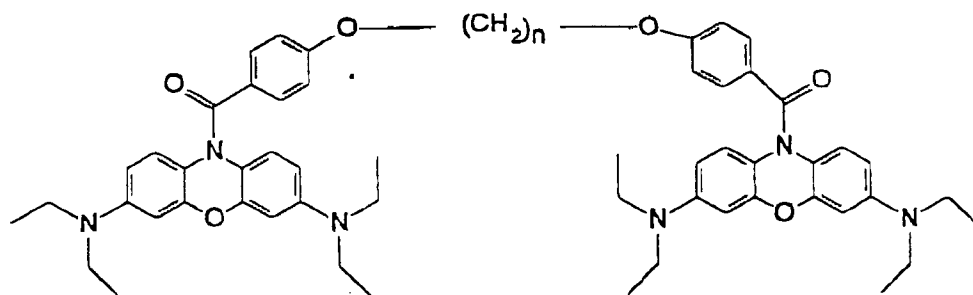
35

40

45

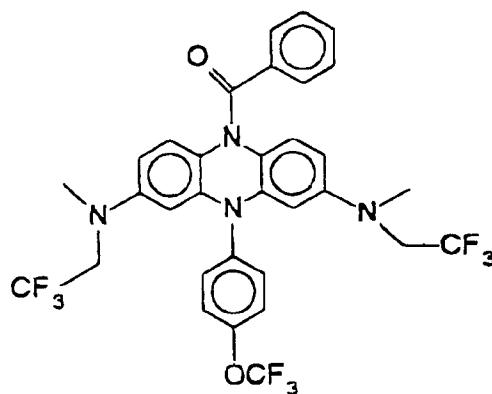
50

55

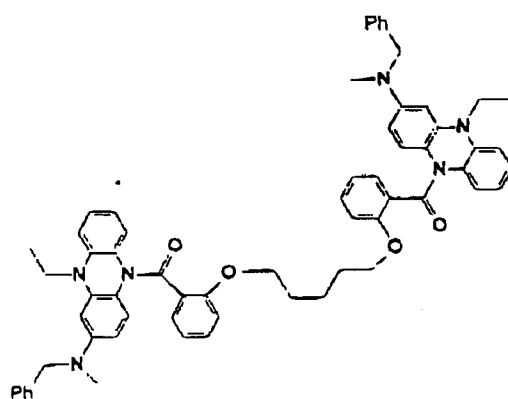


$n = 5$ L2 (cyan)

$n = 10$ L3 (cyan)



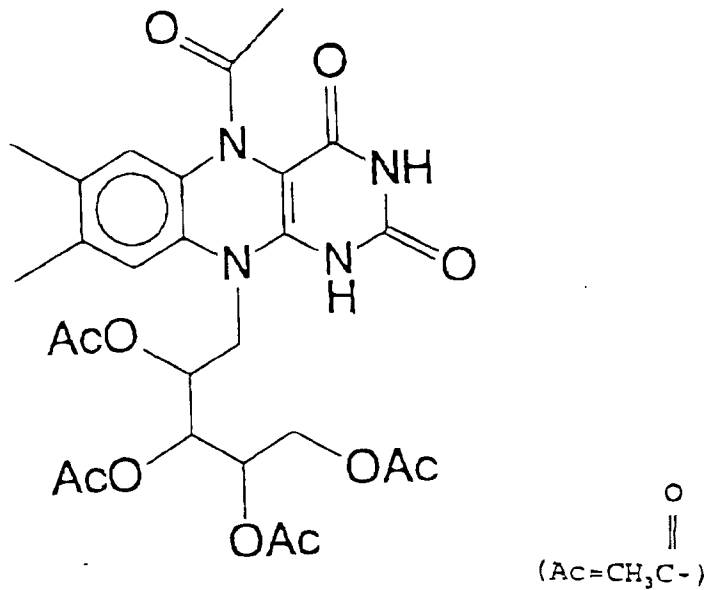
L4 (magenta)



L5 (magenta)

8. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 1, wobei der Leu-

kofarbstoff:



L6 (gelb)

9. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach einem der vorstehenden Ansprüche, wobei entweder:

der IR-Farbstoff und der Leukofarbstoff in derselben Schicht auf einem Substrat vorhanden sind oder
der IR-Farbstoff und der Leukofarbstoff in getrennten Schichten auf dem Substrat aufgetragen sind.

10. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 9, wobei die Farbstoffschicht(en) zusätzlich ein Bindemittel umfaßt (umfassen) das aus Polyvinylbutyral, Vinylharzen und Zelluloseestern ausgewählt ist.

11. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach einem der vorstehenden Ansprüche, wobei der Leukofarbstoff in einer Menge vorhanden ist, die mindestens einem, bevorzugt mindestens drei, molaren Äquivalenten des IR-Farbstoffs entspricht.

12. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach einem der vorstehenden Ansprüche, zusätzlich umfassend ein Silbersalz und einen Entwickler, der in der Lage ist, das Silbersalz zu reduzieren.

13. Durch Laser bildhaft belichtbares direkt beschreibbares Aufzeichnungsmedium nach Anspruch 12, wobei das Silbersalz Silberbehenat und der Entwickler ein sterisch gehindertes Phenol oder ein Alkylester einer Hydroxybenzoesäure ist.

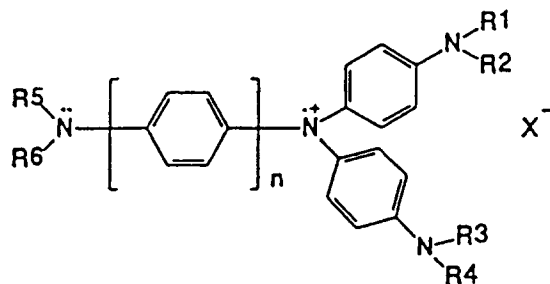
14. Verfahren zur bildhaften Belichtung eines photographischen Materials umfassend die Bestrahlung eines durch Laser bildhaft belichtbaren direkt beschreibbaren Materials nach einem der vorstehenden Ansprüche mit Laserstrahlung.

15. Verfahren zur bildhaften Belichtung eines photographischen Materials nach Anspruch 14, wobei die Laserstrahlung eine Intensität von mindestens 10^{17} Photonen/cm²/s hat.

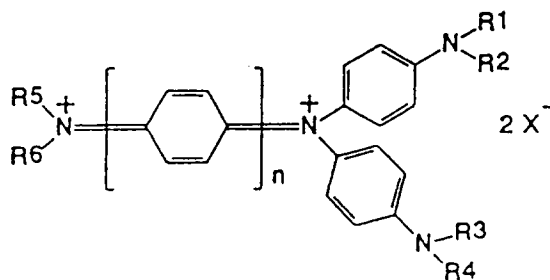
Revendications

- Support à écriture directe pouvant recevoir une image par laser comprenant un colorant infrarouge en association photoréactive à un leuco-colorant₁ dans lequel l'irradiation du support à une longueur d'onde absorbée par ledit colorant infrarouge convertit ledit leuco-colorant en colorant correspondant, caractérisé en ce que ledit colorant infrarouge comprend un chromophore qui est formellement le produit d'une oxydation à un électron ou à deux électrons d'une p-phénylènediamine ou d'une 4,4'-biphénylènediamine.
- Support à écriture directe pouvant recevoir une image par un laser selon la revendication 1, dans lequel ledit colorant infrarouge possède un noyau de formule I(a) ou I(b) ci-dessous:

I (a)



I (b)



dans lesquelles

n vaut 1 ou 2,

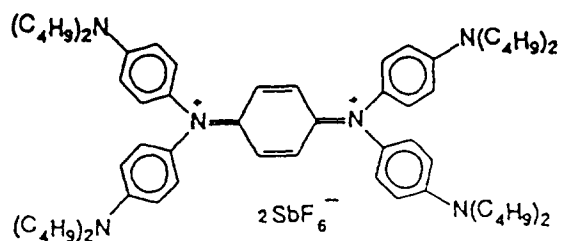
X est un anion dérivé d'un acide fort;

R¹ à R⁴ sont choisis indépendamment parmi H, des groupes alkyle ayant jusqu'à 15 atomes de carbone, des groupes hétérocycliques ayant jusqu'à 10 atomes choisis parmi C, N, O, S, ou bien R¹ conjointement avec R² et/ou R³ conjointement avec R⁴ peuvent compléter une structure cyclique ayant jusqu'à 10 atomes de squelette choisis parmi C, N, O, S, ou bien l'un quelconque parmi R¹ à R⁴ ou R¹ et R² ou R³ et R⁴ peuvent compléter un cycle condensé au noyau phényle auquel l'atome N en question est lié; et

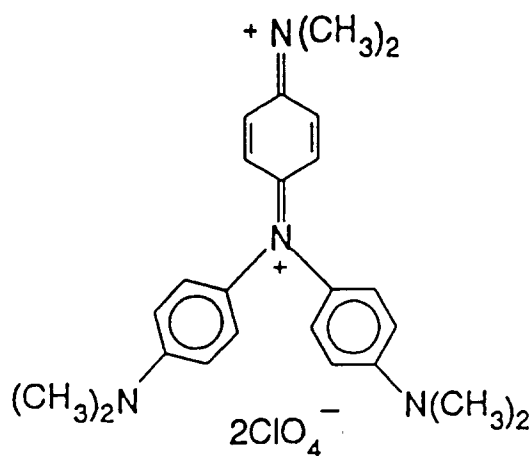
R⁵ et R⁶ représentent indépendamment 4-(R⁷R⁸N)-C₆H₄- (où R⁷ et R⁸ possèdent la même définition que R¹ à R⁴), des groupes alkyle ayant jusqu'à 15 atomes de carbone, des groupes aryle ayant jusqu'à 10 atomes de carbone, des groupes hétérocycliques ayant jusqu'à 10 atomes choisis parmi C, N, O, S ou R⁵ conjointement avec R⁶ peut compléter une structure cyclique ayant jusqu'à 10 atomes de squelette choisis parmi C, N, O, S, ou bien R⁵ et/ou R⁶ peuvent compléter un cycle condensé au noyau phényle auquel R⁵R⁶N est lié.

- Support à écriture directe pouvant recevoir une image par laser selon la revendication 2, dans lequel ledit colorant infrarouge est choisi parmi:

(1)

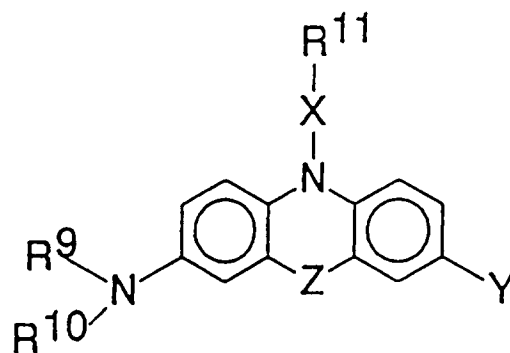


(2)



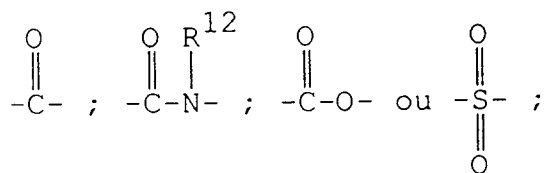
4. Support à écriture directe pouvant recevoir une image par laser selon l'une quelconque des revendications précédentes, dans lequel ledit leuco-colorant est un leuco-colorant protégé, de préférence un dérivé acyle ou sulfonyle.
5. Support à écriture directe pouvant recevoir une image par laser selon la revendication 4, dans lequel ledit leuco-colorant possède un noyau de formule II:

II



dans laquelle

X représente



Y représente H, NR^9R^{10} , un groupe alcoxy, alkylthio, aryloxy, arylthio, alkyle, aryle ou un atome d'halogène;

Z représente O, S ou NR^{13} ;

R^{12} représente H, un groupe alkyle ou aryle;

R^9 , R^{10} et R^{13} sont choisis indépendamment parmi H, des groupes alkyle, aryle, alkylcarbonyle, arylcarbonyle, alkylsulfonyl ou arylsulfonyl, ou bien R^9 et R^{10} représentent les atomes nécessaires à compléter une structure cyclique condensée au noyau ayant des atomes de squelette choisis parmi C, N, O et S; et R^{11} représente tout groupe qui n'empêchera pas un clivage par oxydation de la liaison X-N.

6. Support à écriture directe pouvant recevoir une image par laser selon la revendication 5, dans lequel:

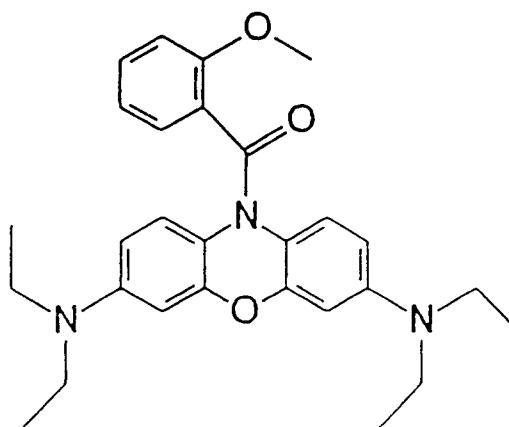
X est un groupe carbonyle

R^{11} est un groupe alkyle ou aryle.

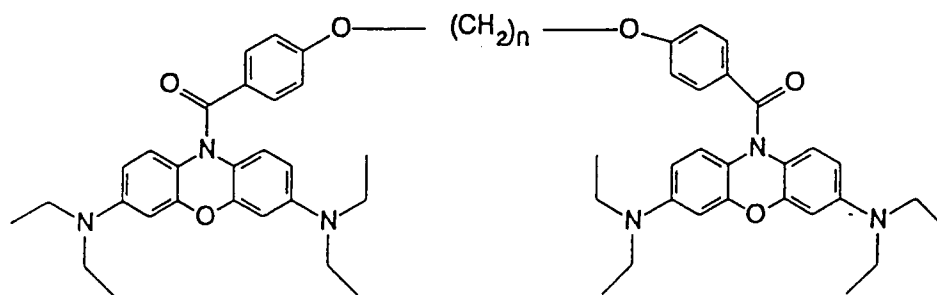
R^9 et R^{10} représentent des groupes alkyle

Y représente NR^9R^{10} et Z représente O ou NR^{13} où R^{13} est un groupe alkyle ou aryle.

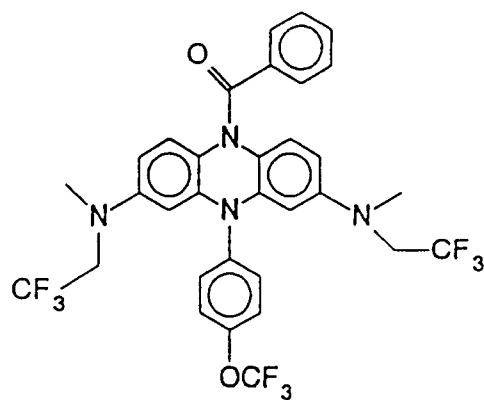
7. Support à écriture directe pour recevoir une image par laser selon la revendication 5, dans lequel ledit leuco-colorant est choisi parmi



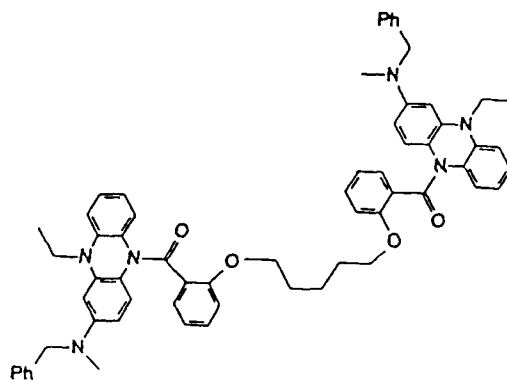
L1 (cyan)



n = 5 L2 (cyan)
n = 10 L3 (cyan)

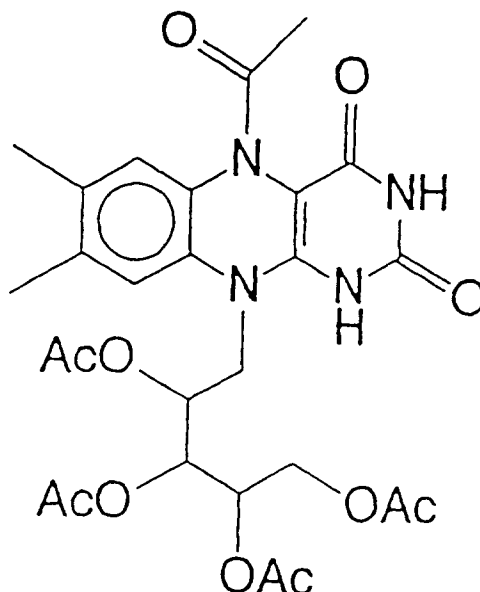


L4 (magenta)

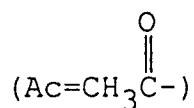


L5 (magenta)

8. Support à écriture directe pouvant recevoir une image par laser selon la revendication 1, dans lequel ledit leuco-colorant est :



L6 (jaune)



9. Support à écriture directe pouvant recevoir une image par laser selon l'une quelconque des revendications précédentes, dans lequel:

ledit colorant IR et ledit leuco-colorant sont présents dans la même couche sur un substrat ou bien
ledit colorant IR et ledit leuco-colorant sont déposés dans des couches séparées sur un substrat.

10. Support à écriture directe pouvant recevoir une image par laser selon la revendication 9, dans lequel ladite ou lesdites couches de colorant comprennent de plus un liant choisi parmi le polyvinylbutyral, les résines vinyliques et les esters celluloseux.

11. Support à écriture directe pouvant recevoir une image par laser selon l'une quelconque des revendications précédentes, dans lequel ledit leuco-colorant est présent en une quantité correspondant à au moins un, de préférence au moins trois, équivalents molaires du colorant IR.

12. Support à écriture directe pour recevoir une image par laser selon l'une quelconque des revendications précédentes, comprenant de plus un sel d'argent et un révélateur capable de réduire ledit sel d'argent.

13. Support à écriture directe pour recevoir une image par laser selon la revendication 12, dans lequel ledit sel d'argent est le bérénate d'argent et ledit révélateur est un phénol encombré ou un ester alkylique d'acides hydroxybenzoïques.

14. Procédé de formation d'images sur un support photographique consistant à exposer un support à écriture directe pouvant recevoir une image par laser selon l'une quelconque des revendications précédentes à une irradiation par laser.

15. Procédé de formation d'images sur un support photographique selon la revendication 14, dans lequel ladite irradiation

tion par laser possède une intensité d'au moins 10^{17} photons/cm²/s.

5

10

15

20

25

30

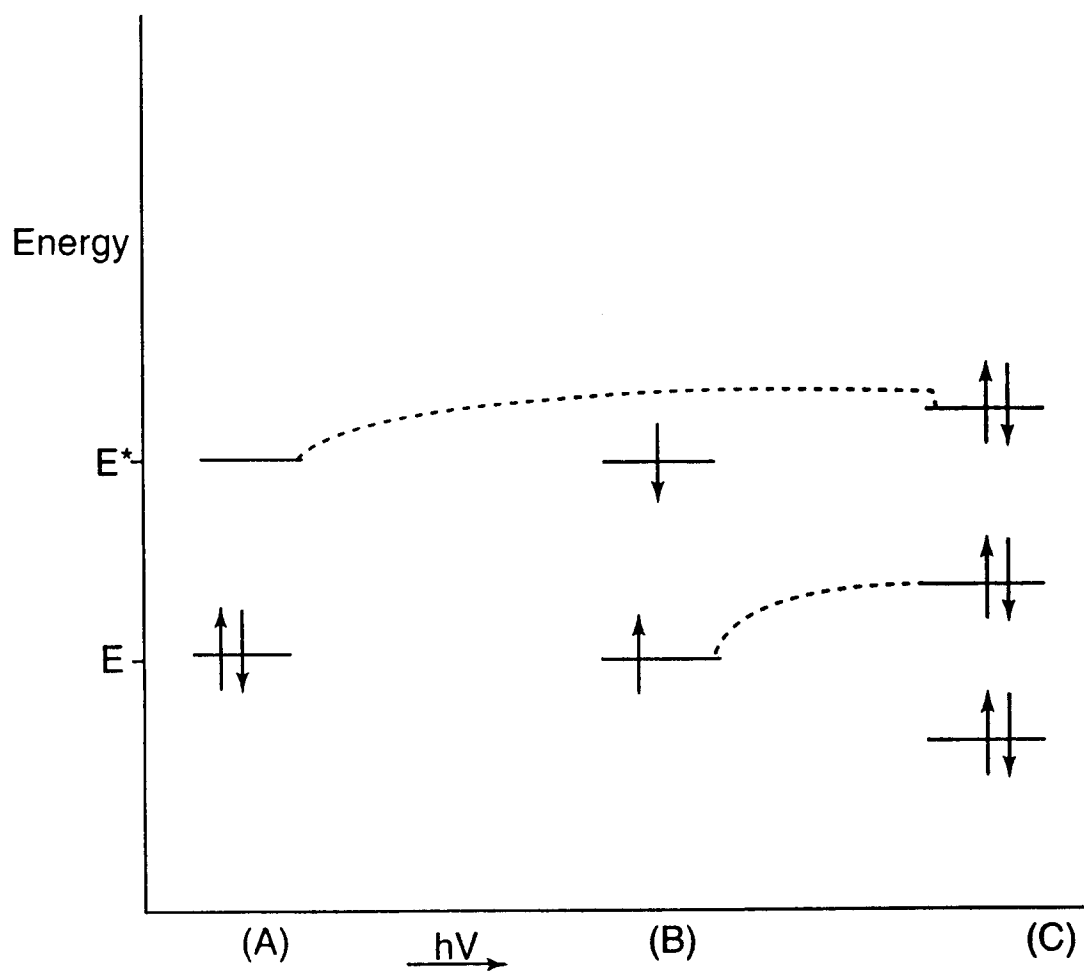
35

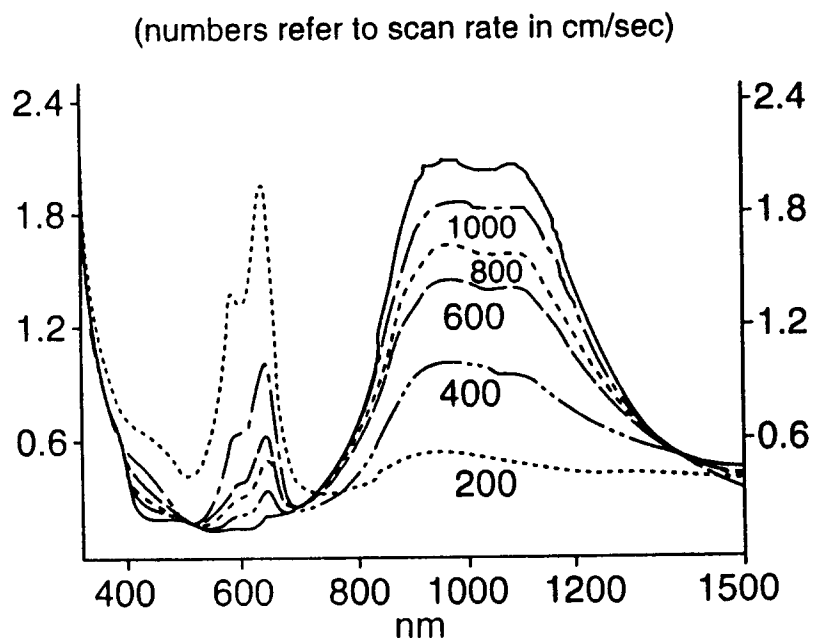
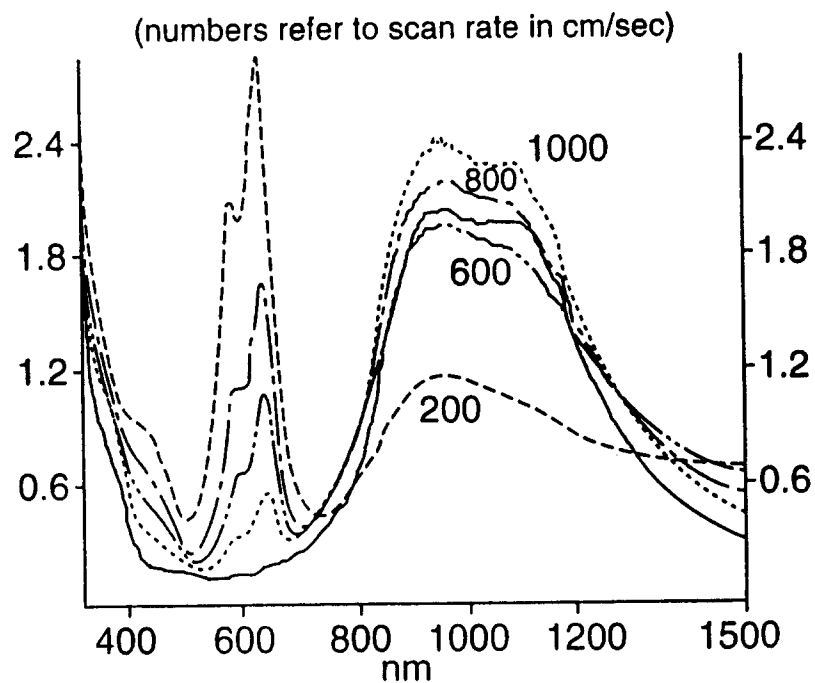
40

45

50

55

**Fig. 1**

**Fig. 2a****Fig. 2b**