



(11) **EP 0 908 306 B3**

(12) **NEW EUROPEAN PATENT SPECIFICATION**
After limitation procedure (B3-1)

(45) Date of publication and mention of the limitation decision: **B3-1 05.08.2009 Bulletin 2009/32**

(51) Int Cl.: **B41C 1/10** (2006.01) **B41M 5/36** (2006.01)

(45) Mention of the grant of the patent: **13.02.2002 Bulletin 2002/07**

(21) Application number: **98203121.3**

(22) Date of filing: **16.09.1998**

(54) **A method for making positive working printing plates from a heat mode sensitive imaging element**

Verfahren zur Herstellung einer positiv arbeitenden Druckplatte aus wärmempfindlichem Bildaufzeichnungsmaterial

Procédé pour la fabrication d'une plaque d'impression positive à partir d'un élément pour l'enregistrement de l'image thermosensible

(84) Designated Contracting States:
BE DE FR GB

(30) Priority: **08.10.1997 EP 97203129**

(43) Date of publication of application:
14.04.1999 Bulletin 1999/15

(73) Proprietor: **AGFA-GEVAERT**
2640 Mortsel (BE)

(72) Inventors:
• **Van Damme, Marc**
2640 Mortsel (BE)

• **Vermeersch, Joan**
2640 Mortsel (BE)
• **Deroover, Geert**
2640 Mortsel (BE)

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EP-A- 0 347 245 **EP-A- 0 366 461**
EP-A- 0 573 092 **EP-A- 0 706 899**
EP-A- 0 732 628 **WO-A-95/07822**
DE-A- 4 331 162 **GB-A- 1 076 799**
GB-A- 1 154 568 **GB-A- 1 155 035**
GB-A- 1 160 221 **GB-A- 1 245 924**
US-A- 5 466 557 **US-A- 5 491 046**

EP 0 908 306 B3

Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a method for preparing a lithographic printing plate using a heat mode imaging element comprising an IR sensitive top layer.

[0002] More specifically the invention is related to a method for preparing a lithographic printing plate using a heat mode imaging element whereby the capacity of the top layer of being penetrated and/or solubilised by an aqueous developer is changed upon exposure.

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BACKGROUND OF THE INVENTION

[0003] Lithography is the process of printing from specialty prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

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[0004] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophilic background.

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[0005] In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazosensitized systems are widely used.

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[0006] Upon imagewise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

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[0007] Alternatively, printing plates are known that include a photosensitive coating that upon image-wise exposure is rendered soluble at the exposed areas. Subsequent development then removes the exposed areas. A typical example of such photosensitive coating is a quinone-diazide based coating.

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[0008] Typically, the above described photographic materials from which the printing plates are made are camera-exposed through a photographic film that contains the image that is to be reproduced in a lithographic printing process. Such method of working is cumbersome and labor intensive. However, on the other hand, the printing plates thus obtained are of superior lithographic quality.

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[0009] Attempts have thus been made to eliminate the need for a photographic film in the above process and in particular to obtain a printing plate directly from computer data representing the image to be reproduced. However the photosensitive coating is not sensitive enough to be directly exposed with a laser. Therefore it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide can then directly be exposed by means of a laser under the control of a computer. Subsequently, the silver halide layer is developed leaving a silver image on top of the photosensitive coating. That silver image then serves as a mask in an overall exposure of the photosensitive coating. After the overall exposure the silver image is removed and the photosensitive coating is developed. Such method is disclosed in for example JP-A- 60- 61 752 but has the disadvantage that a complex development and associated developing liquids are needed.

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[0010] GB-1 492 070 discloses a method wherein a metal layer or a layer containing carbon black is provided on a photosensitive coating. This metal layer is then ablated by means of a laser so that an image mask on the photosensitive layer is obtained. The photosensitive layer is then overall exposed by UV-light through the image mask, After removal of the image mask, the photosensitive layer is developed to obtain a printing plate. This method however still has the disadvantage that the image mask has to be removed prior to development of the photosensitive layer by a cumbersome processing.

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[0011] Furthermore methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat mode printing plate precursors is clearly seen on the market.

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[0012] For example, **Research Disclosure no. 33303** of January 1992 discloses a heat mode imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink-acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, undercritical

conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.

5 [0013] US-P- 4 708 925 discloses imaging elements including a photosensitive composition comprising an alkali-soluble novolac resin and an onium-salt. This composition can optionally contain an IR-sensitizer. After image-wise exposing said imaging element to UV - visible - or IR-radiation followed by a development step with an aqueous alkali liquid there is obtained a positive or negative working printing plate. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

10 [0014] EP-A- 625 728 discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which can be positive or negative working. This layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

15 [0015] US-P- 5 340 699 is almost identical with EP-A- 625 728 but discloses the method for obtaining a negative working IR-laser recording imaging element. The IR-sensitive layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0016] Furthermore EP-A- 678 380 discloses a method wherein a protective layer is provided on a grained metal support underlying a laser-ablatable surface layer. Upon image-wise exposure the surface layer is fully ablated as well as some parts of the protective layer. The printing plate is then treated with a cleaning solution to remove the residu of the protective layer and thereby exposing the hydrophilic surface layer.

20 [0017] GB-A-1 245 924 discloses an information recording method wherein a recording material is used comprising a heat-sensitive recording layer of a composition such that the solubility of any given area of the layer in a given solvent can be increased by heating that area of the layer, wherein the said layer is information-wise heated to produce a record of the information in terms of a difference in the solubilities in the said solvent of different areas of the recording layer, and wherein the whole layer is then contacted with such solvent to cause the portions of the recording layer which are

25 soluble or most soluble in such solvent to be removed or penetrated by such solvent.
[0018] EP-A-347 245 discloses a method for development-processing of presensitized plates for use in making lithographic printing plates which comprises imagewise exposing the presensitized plate to light and development-processing the exposed presensitized plate with an alkaline developer and a replenisher, wherein the developer and the replenisher are aqueous solutions of an alkali metal silicate and the ratio (SiO₂) : (M₂O) (wherein (SiO₂) and (M₂O) are the molar concentrations of respectively SiO₂ and an alkali metal oxide M₂O) of the replenisher ranges from 0.6 to 1.5.

30 [0019] US-P- 5 466 557 discloses a radiation-sensitive composition comprising (1) a resole resin, (2) a novolac resin, (3) a latent Bronsted acid, (4) an infrared absorber, and (5) terephthalaldehyde.

35 [0020] GB-A-1155 035 discloses a method of recording information, wherein a recording material is used comprising a layer of a polymeric material which when any given area of the layer is sufficiently heated undergoes in that area a modification resulting in a decrease in the solubility of that area of the layer in water or an aqueous medium, such layer also incorporating a substance or substances distributed over the whole area of the layer and being capable of being heated by exposing the layer to intense radiant energy which is absorbed by such substance or substances, and wherein the said material is exposed to intense radiant energy which is distributed over the material in a pattern determined by the information to be recorded and which is at least partly absorbed by said distributed substance or substances, so

40 that a corresponding heat pattern is generated in the material, whereby such information is recorded in terms of a difference in the solubilities in water or an aqueous medium of different areas of said layer.
[0021] GB-A- 1 154 568 discloses a method of recording a graphic original having contrasting light-absorbing and light-transmitting areas, wherein a recording material comprising a supported layer composed mainly of gelatin the water-solubility or water-absorptive capacity of which increases if the layer is sufficiently heated , such layer also having light absorbing substance(s) distributed therein, is placed with such gelatin layer in contact with the light-absorbing areas of the original and the said gelatin layer is exposed to light through the original, the intensity of the light and the duration of the exposure being such that the areas of the gelatin layer in contact with the light-absorbing areas of the original are substantially unaffected by heat conduction from such light-absorbing areas, but the water-solubility or water-absorptive capacity of the other areas of the gelatin layer is increased by heating thereof due to absorption of copying light by the

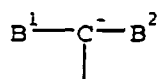
50 light-absorbing substance(s) in those other areas of the gelatin layer.
[0022] So, there is a need for a heat-mode imaging element which is easy to prepare and which undergoes little or no ablation during the IR-radiation.

OBJECTS OF THE INVENTION

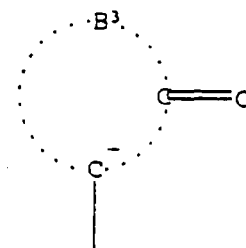
55 [0023] It is an object of the invention to provide a method for making lithographic printing plates from heat mode imaging elements which are easy to prepare.

[0024] It is a further object of the invention to provide a method for making lithographic printing plates from a heat

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can be represented by



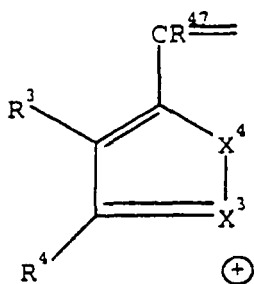
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wherein B³ represents the non-metal atoms to complete a carbocyclic or heterocyclic ring,
ring T can be substituted by 1 to 3 C₁ - C₄ alkyl groups, n = 1 or 2,
and A¹ and A² can represent following combinations :

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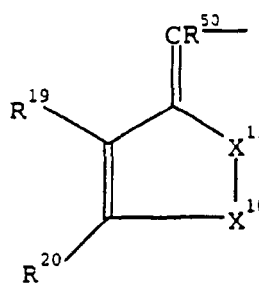
(1) moieties of formulas (IIIa) and (IIIb) :

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(IIIa)

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(IIIb)

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wherein X³, X¹⁰ = O,X⁴, X¹¹ = -CR³⁸ = -CR³⁹,

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R³⁸ and R³⁹ each independently represent hydrogen, alkyl, aryl or together the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5 or 7 membered ring, or independently from each other, the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5- or 7-membered ring,

and R³, R⁴, R¹⁹ and R²⁰ each independently represent hydrogen, C₁ - C₈ alkyl, aryl, halogen, cyano, alkoxy, carbonyl, optionally substituted aminocarbonyl, amino, monoalkylamino, dialkylamino, hydroxy, alkoxy, aryloxy, alkylthio, arylthio, acyloxy, acylamino, arylamino, alkylcarbonyl, arylcarbonyl, or the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5- or 7-membered ring,

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R⁴⁷ and R⁵⁰ each independently represent hydrogen, alkyl, aryl, cyano, alkoxy, cyano or the non-metal atoms to form a saturated or unsaturated 5- to 7-membered ring, in the first case between R⁴⁷ and resp. X⁴ and R³, in the second case between R⁵⁰ and resp. X¹¹ and R¹⁹,

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(2) moieties of the same formulas (IIIa) and (IIIb)

wherein X³, X¹⁰ = R⁴⁴N,X⁴, X¹¹ = -CR³⁸ = -CR³⁹,

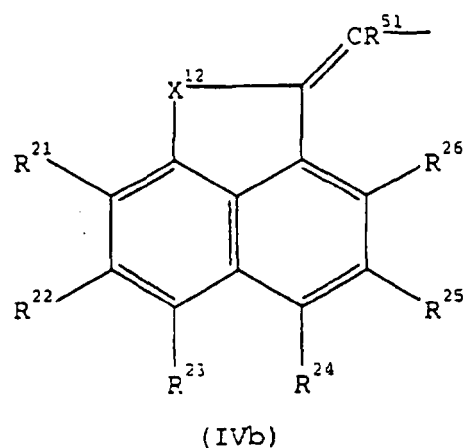
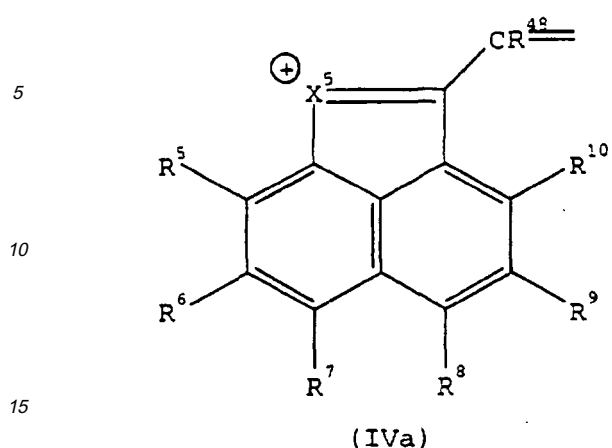
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and wherein R³ and R⁴, respectively R³⁸ and R³⁹ together represent the atoms to complete an optionally substituted aromatic ring,

and wherein R⁴⁴ represents optionally substituted alkyl or aryl, or the necessary atoms to complete a 5- or 7-membered ring,

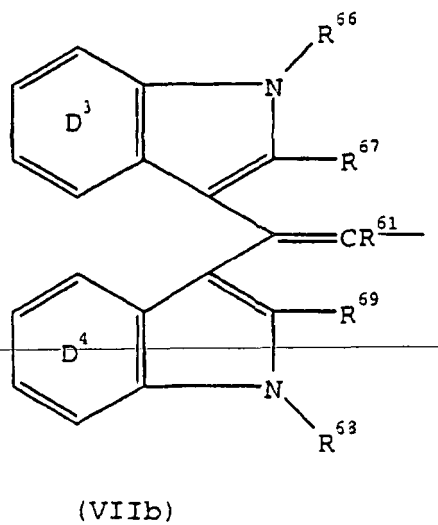
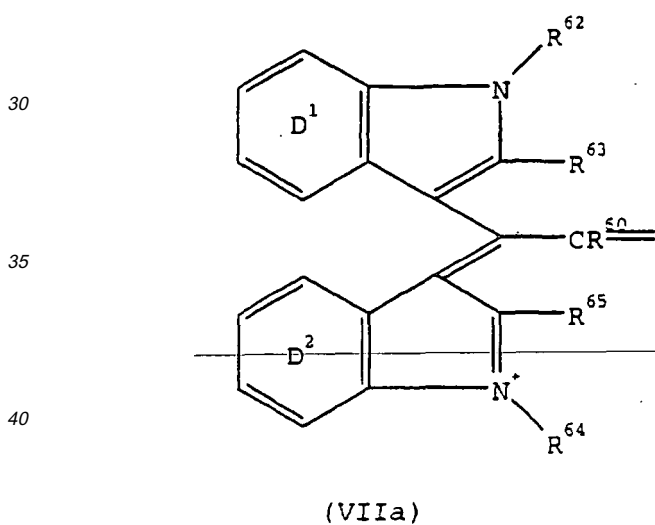
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(3) moieties of the formulas (IVa) and (IVb) :



20 wherein X^5 and X^{12} each independently represent O, S, Se, Te or $R^{44}N$,
 R^5 to R^{10} and R^{21} to R^{26} each independently represent one of the meanings given above for R^3 , and R^{48} and R^{51}
 each independently represent hydrogen, alkyl, aryl or alkoxy, carbonyl,
 with the exception for those compounds in which together X^5 , $X^{12} = R^{44}N$ and $Q = \text{halogen}$,

25 (4) moieties of formulas (VIIa) and (VIIb)



45 wherein R^{60} and R^{61} each independently represent hydrogen, alkyl, aryl, cyano, alkoxy, carbonyl, halogen, R^{62} , R^{64} , R^{66}
 R^{68} each independently represent alkyl or aryl,
 R^{63} , R^{65} , R^{67} , R^{69} each independently represent hydrogen, alkyl or aryl,
 and wherein the rings D^1 to D^4 each independently can be substituted once or frequently by hydrogen, chlorine, bromine,
 50 alkyl, or alkoxy.

[0033] Most preferred subclasses of this general formula (I) are the following :

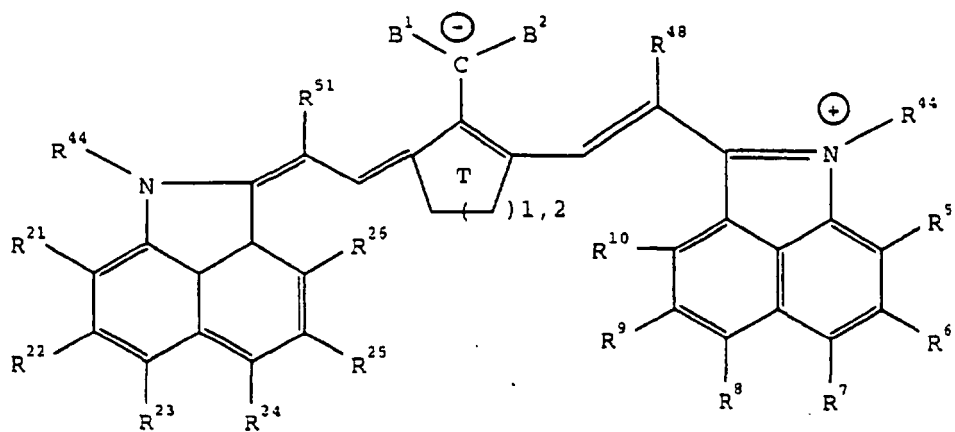
- compounds according to formula (XXI)

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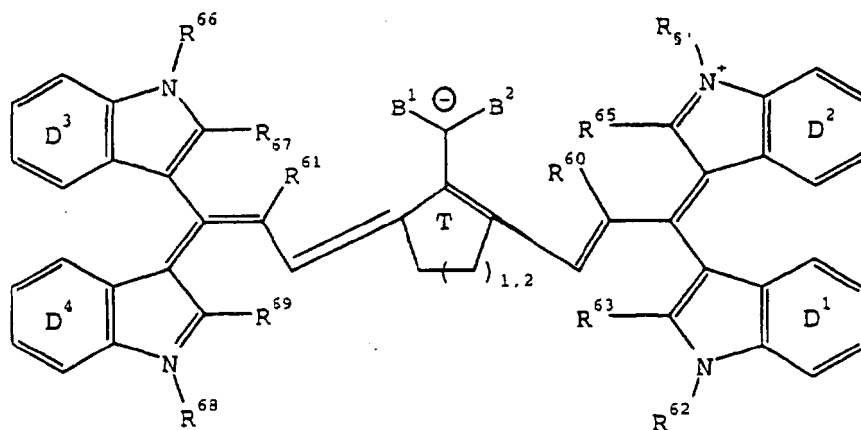
(XXI)

20 - compounds according to formula (XXIII) :

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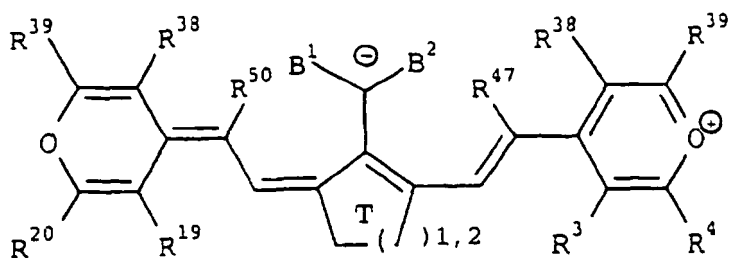
(XXIII)

40 - compounds according to formula (XXV) :

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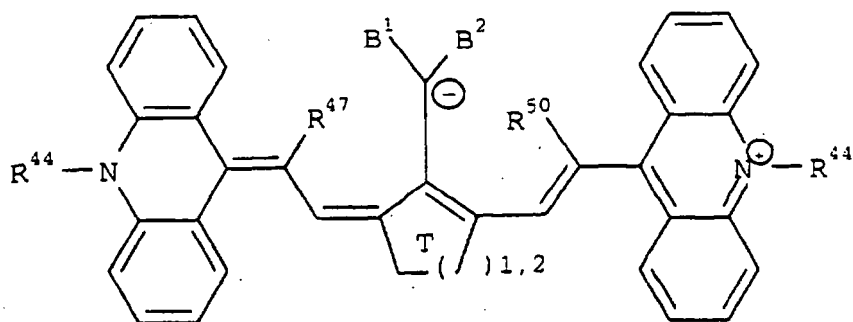
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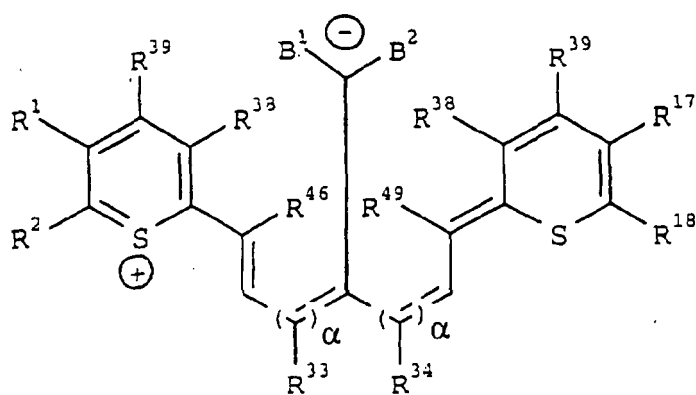
(XXV)

- compounds according to formula (XXVII)



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- compounds according to formula (XXIX) :



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[0034] In the formulas of these subclasses R1, R2, R17 and R18 have the same meaning as R3, and B1, B2, the other R symbols, T, and the D symbols are defined as hereinbefore, and a is 0 or 1.

[0035] Some specific infra-red absorbing dyes (IRD) corresponding to general formula (I) or to one of the preferred subclasses defined above which are chosen for the determination of specific spectral characteristics are listed below. A reference number is designated to them by which they will be identified in the tables furtheron of the description and examples :

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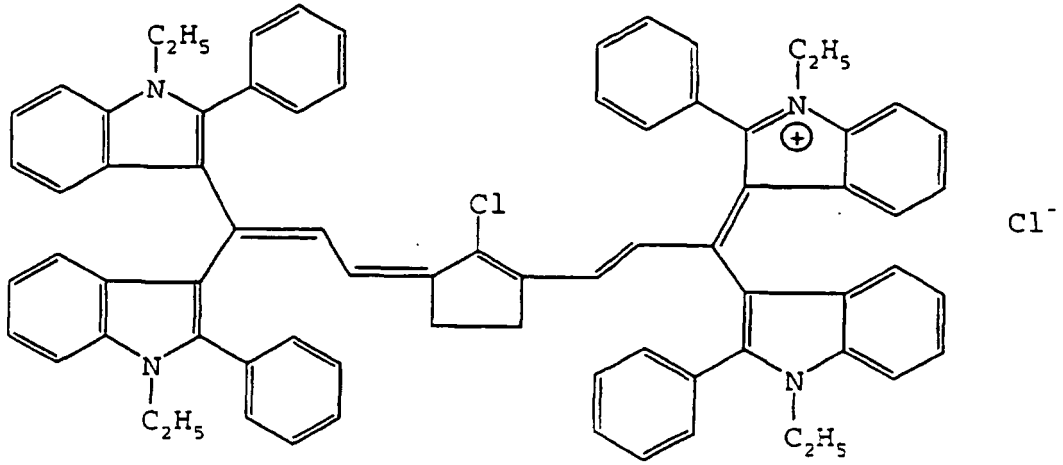
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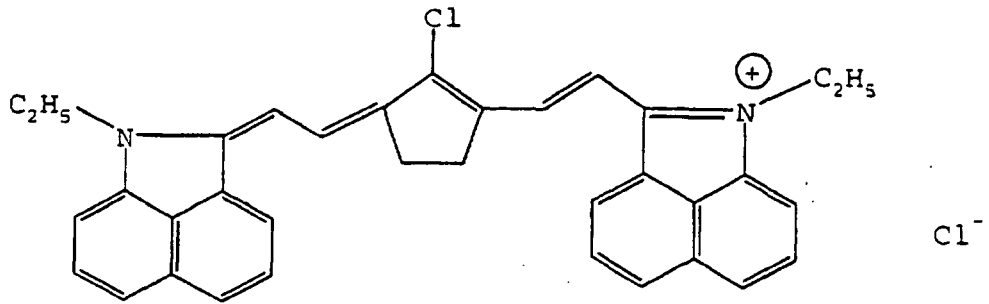


IRD No. 1

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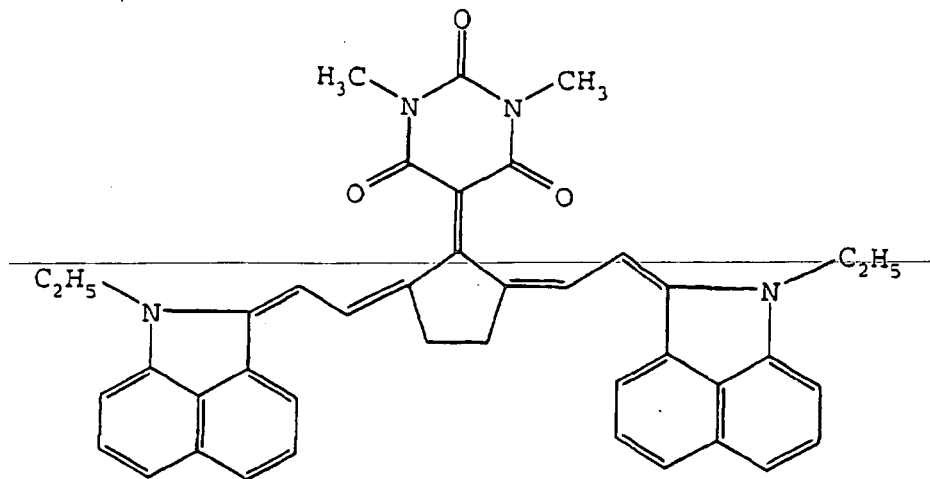
IRD No. 2

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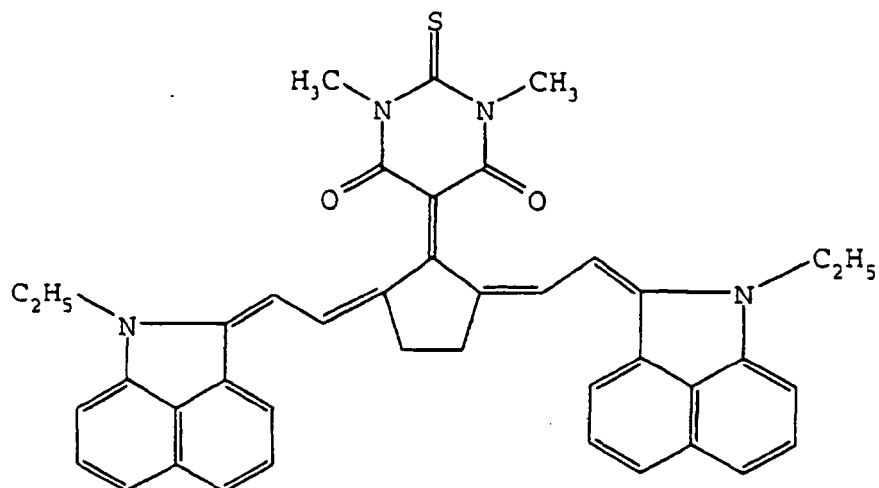
IRD No. 3

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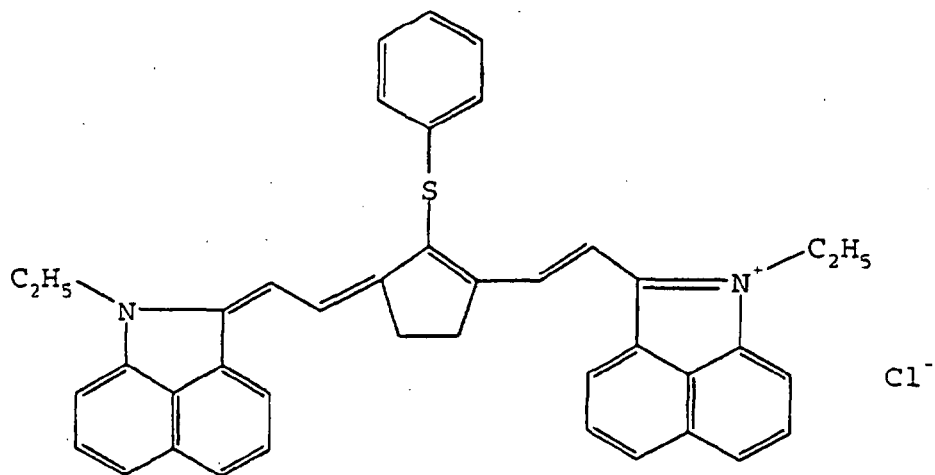
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IRD No. 4

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IRD No. 5

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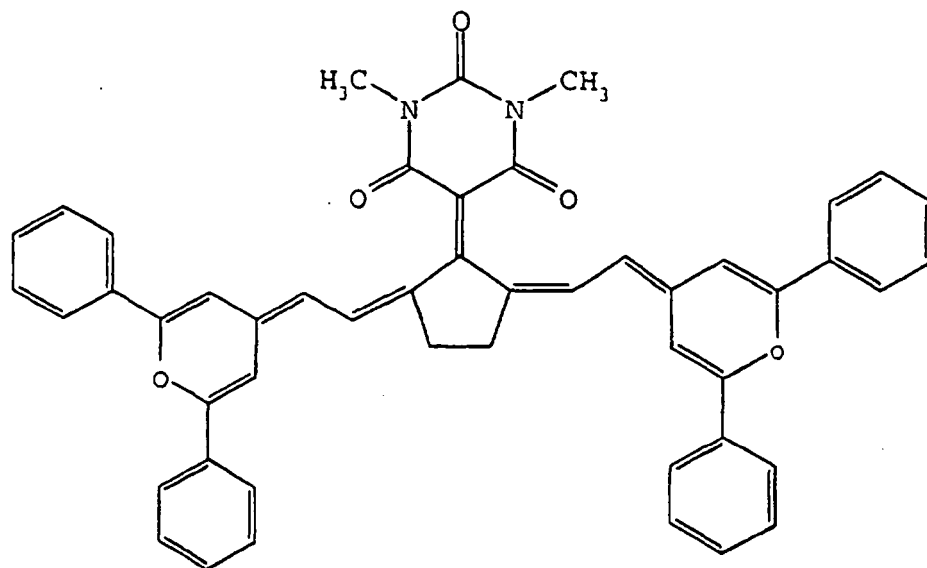
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IRD No. 6

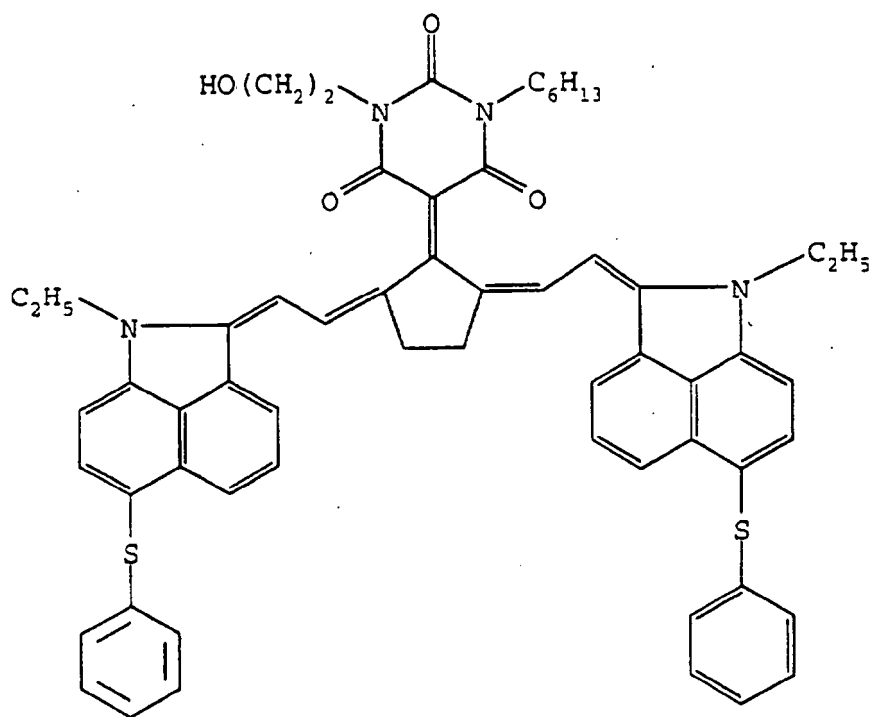
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IRD No. 7

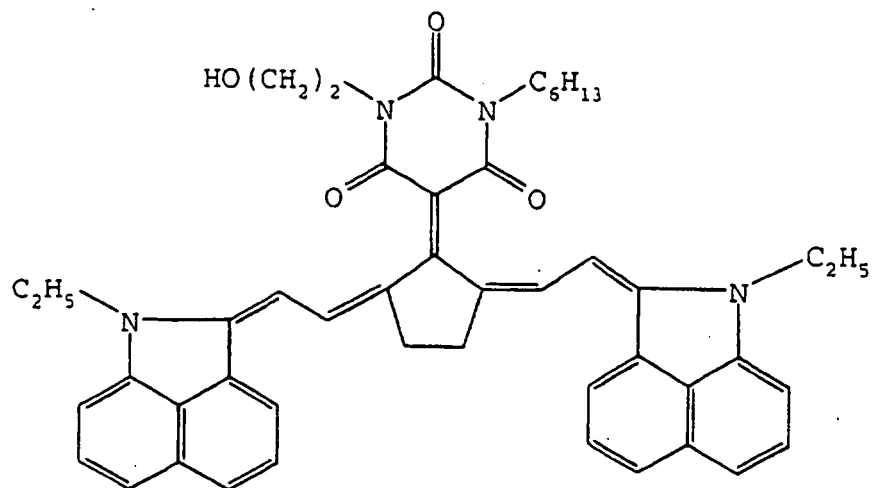
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IRD No. 8

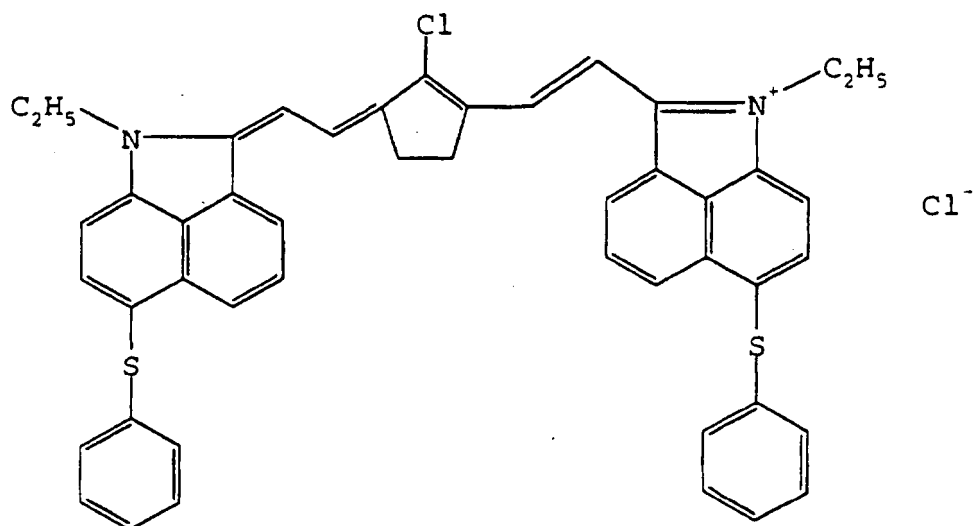
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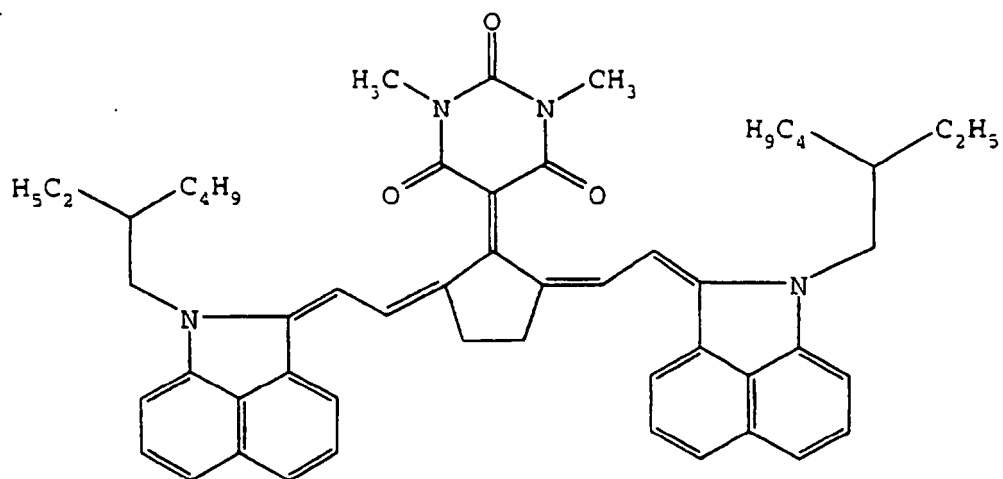


IRD No. 9

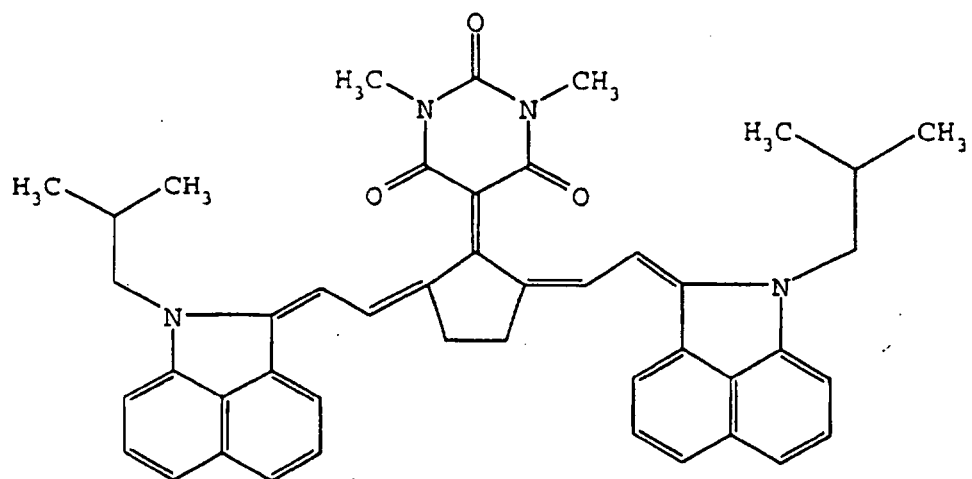
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IRD No. 10

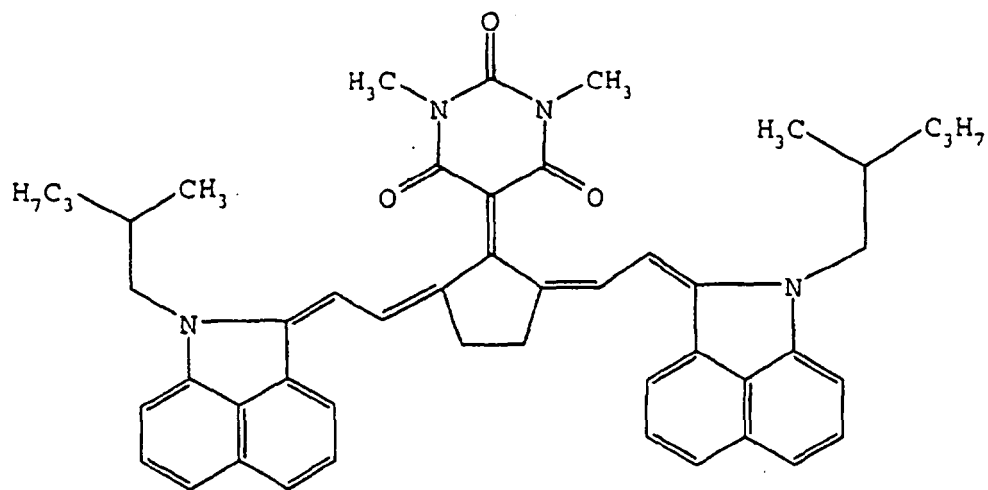


IRD No. 11

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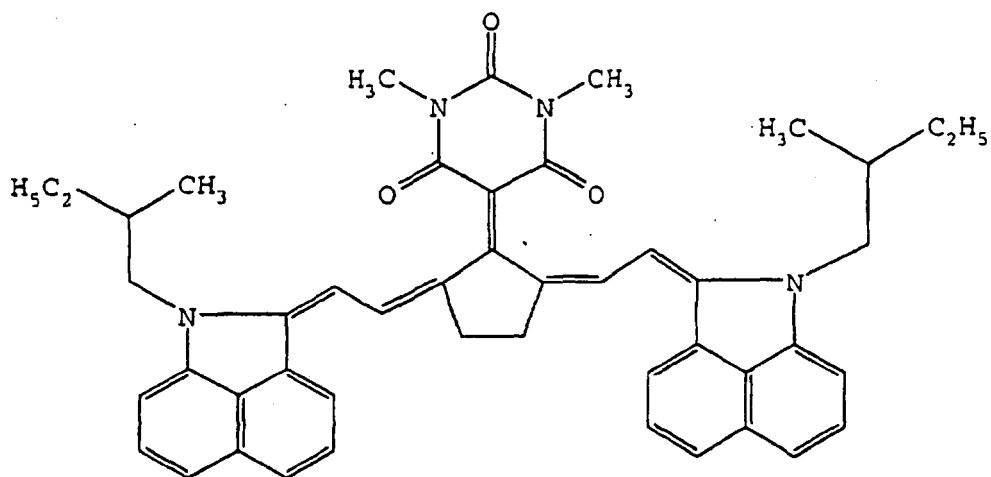
IRD No. 12

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IRD No. 13

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[0036] Further suitable prior art dyes included in the experimental investigation of spectral parameters are represented by following formulas:

[0037] IRD-14 is a commercial product known as CYASORB IR165, marketed by American Cyanamid Co, Glendale Protective Technologie Division, Woodbury, New-York. It is a mixture of two parts of the molecular non-ionic form (IRD-14a) and three parts of the ionic form (IRD-14b) represented by:

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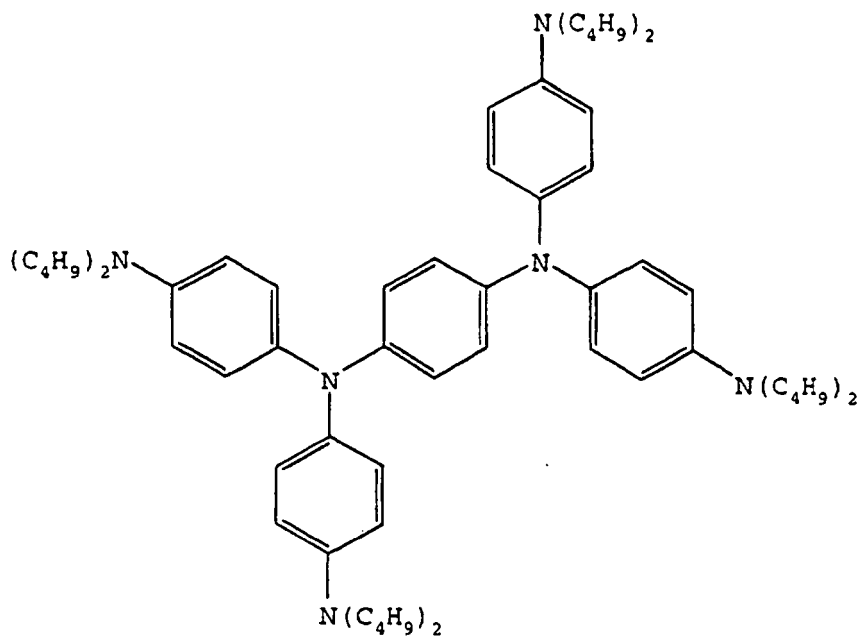
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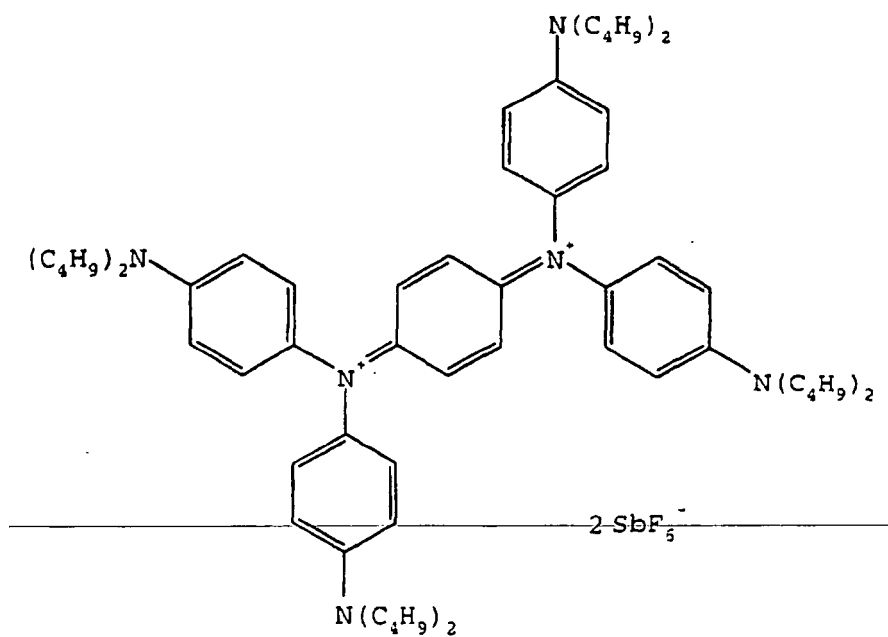
IRD No. 14a

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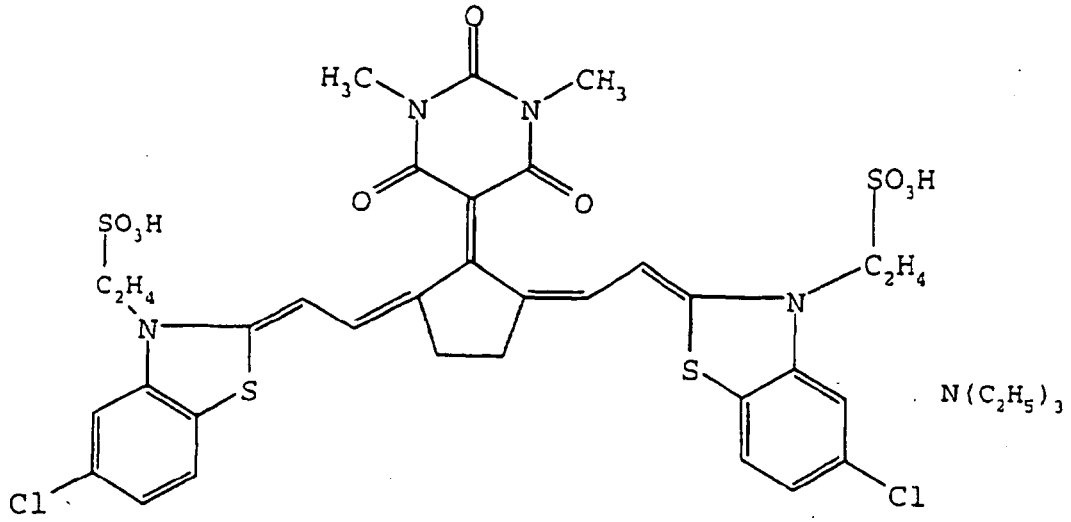
IRD No. 14b

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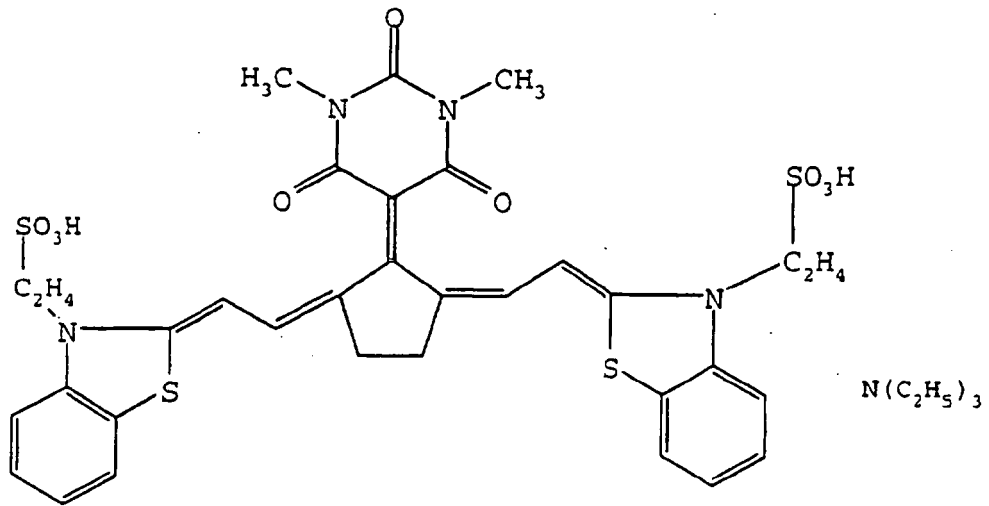
IRD No. 15

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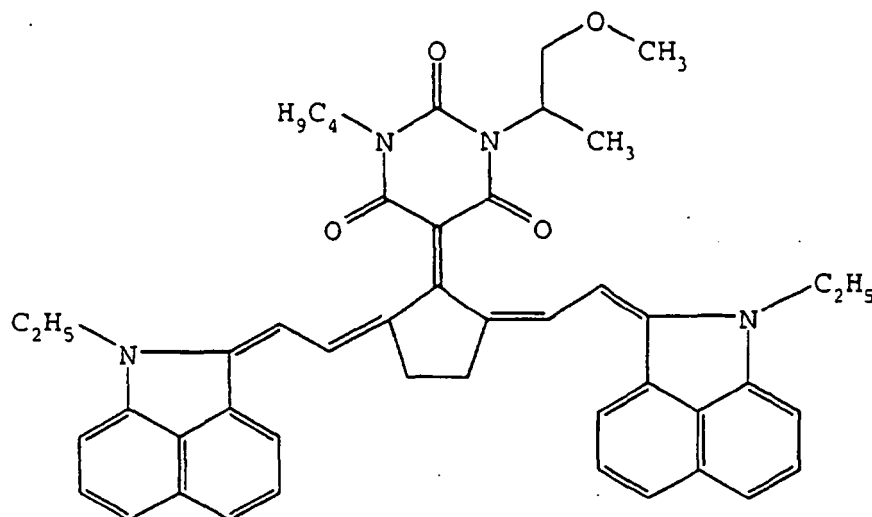


IRD No. 16

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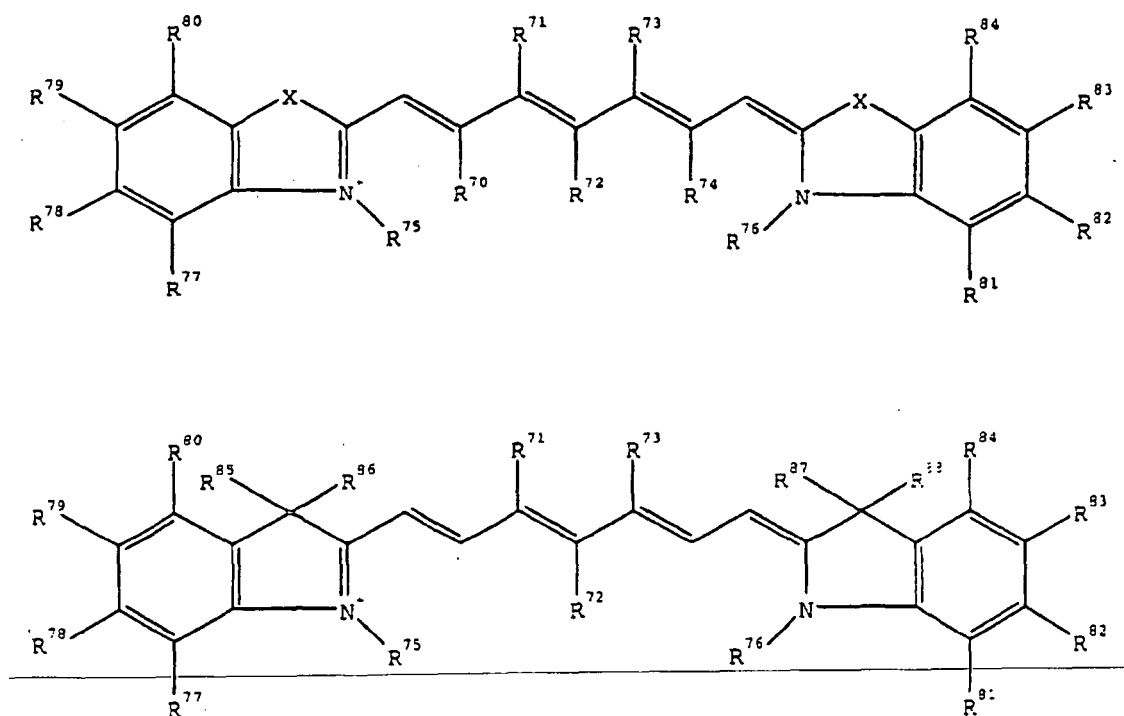
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IRD No. 17

[0038] Other preferred IR-dyes, especially for irradiation with a laser source with an emission spectrum of about 830 nm belong to the scope of the following general formulas.



wherein X, X' each independently represents O, S

R⁷⁰-R⁷⁴ each independently may represent hydrogen, alkyl or aryl; R⁷⁰ together with R⁷², R⁷² together with R⁷⁴, R⁷¹ together with R⁷³, R⁷⁰ together with R⁷² and R⁷⁴ may form a carbocyclic ring.

R⁷² may also represents halogen, NR⁸⁸R⁸⁹ (R⁸⁸, R⁸⁹ each independently represents alkyl, aryl, or may form a (hetero) cyclic ring), PR⁸⁸R⁸⁹, ester-COOR⁹² (R⁹² represents alkyl, or aryl), barbituric acid group (with optionally substituted N-atoms).

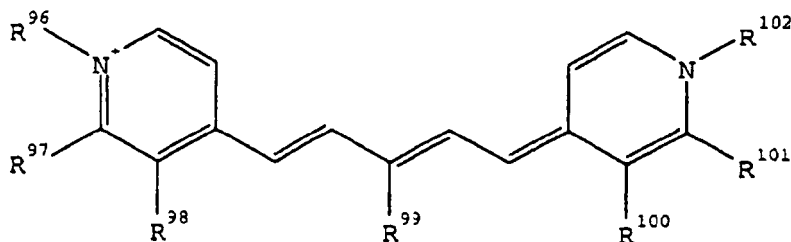
R⁷¹ or R⁷³ may represents : -OCOR⁹³; R⁹³ represents alkyl, or aryl. R⁷⁷ together with R⁷⁸, R⁷⁸ together with R⁷⁹, R⁷⁹ together with R⁸⁰, R⁸¹ together with R⁸², R⁸² together with R⁸³, R⁸³ together with R⁸⁴ may form an annulated benzoring

optionally substituted with a carbocyclic acid, ester or sulphogroup.

R⁷⁸, R⁷⁹, R⁸², R⁸³ each independently may represent hydrogen, alkyl, aryl, halogen, ester, carbocyclic acid, amide, amine, nitrile, alkoxy, aryloxy, or sulpho group.

R⁸⁵, R⁸⁶, R⁸⁷, R⁸⁸ each independently may represent an alkylgroup, R⁸⁵ together with R⁸⁶, R⁸⁷ together with R⁸⁸ may form a cyclic (spiro)ring.

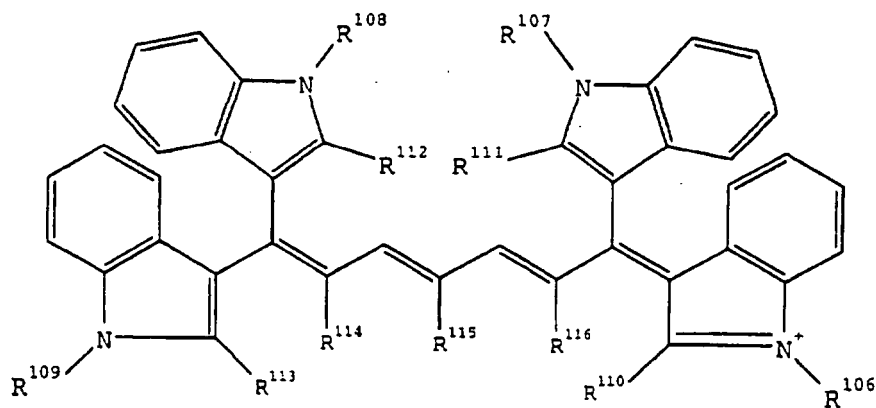
R⁷⁵, R⁷⁶ each independently represents an alkyl, aryl group; -C_nH_{2n}SO₃M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C_nH_{2n}COOR⁹⁴ (n represents an integer from 1 to 5 and R⁹⁴ alkyl, or aryl group); -L1-CONHSO₂R⁹⁵ (L1 represents -C_nH_{2n}- with n an integer from 1 to 4 and R⁹⁵ alkyl or aryl).



R⁹⁶, R¹⁰² represents alkyl, or aryl group; -C_nH_{2n}SO₃M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C_nH_{2n}COOR¹⁰³ (n represents an integer from 1 to 5 and R¹⁰³ alkyl, or aryl group); -L1-CONHSO₂R¹⁰⁴ (L1 represents -C_nH_{2n}- with n an integer from 1 to 4 and R¹⁰⁴ alkyl or aryl).

R⁹⁷, R⁹⁸, R¹⁰⁰, R¹⁰¹ may each independently represent: hydrogen, alkyl, aryl; R⁹⁷ together with R⁹⁸, R¹⁰⁰ together with R¹⁰¹ may form an annulated benzoring.

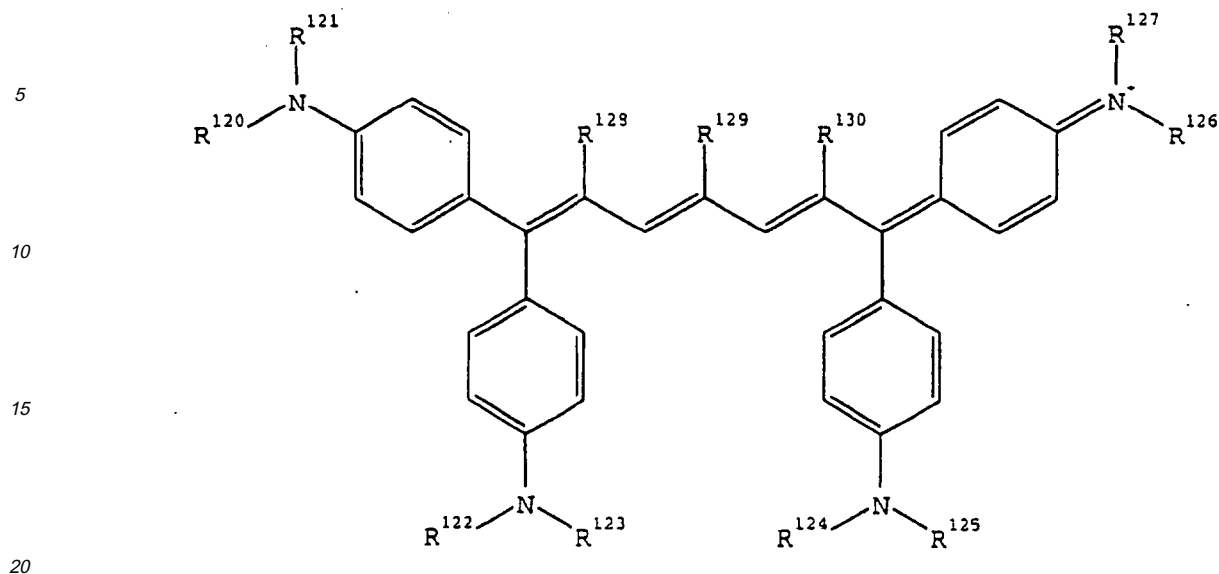
R⁹⁸ may represent: hydrogen, alkyl, aryl, halogen, ester, or -SO₂R¹⁰⁵ (R¹⁰⁵ represents an alkyl or aryl).



R¹⁰⁶, R¹⁰⁷, R¹⁰⁸, R¹⁰⁹ each independently may represent alkyl, aryl group; -C_nH_{2n}SO₃M represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C_nH_{2n}COOR¹¹⁷ (n represents an integer from 1 to 5 and R¹¹⁷ alkyl, or aryl group); -L1-CONHSO₂R¹¹⁸ (L1 represents -C_nH_{2n}- with n an integer from 1 to 4 and R¹¹⁸ alkyl or aryl).

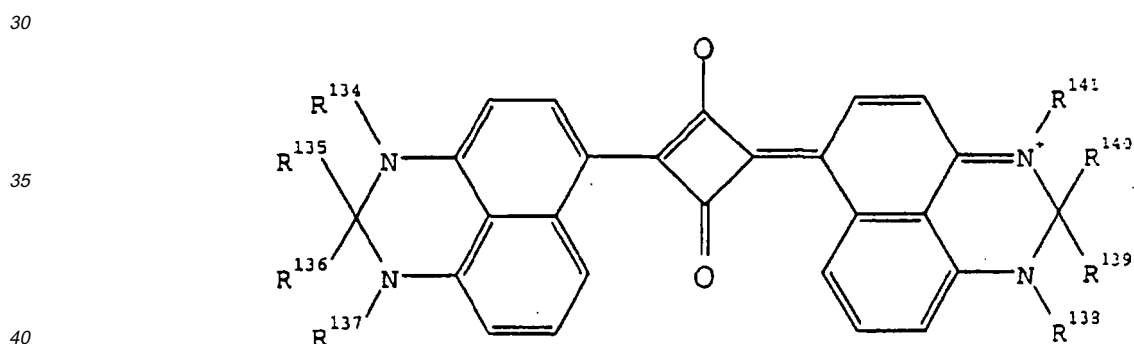
R¹¹⁰, R¹¹¹, R¹¹², R¹¹³ each independently represents : hydrogen, alkyl, or aryl group.

R¹¹⁴, R¹¹⁵, R¹¹⁶ each independently may represent : hydrogen, alkyl, or aryl group; R¹¹⁵ represents halogen, ester, or-SO₂R¹¹⁹ (R¹¹⁹ represents alkyl, or aryl).



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R¹²⁰, R¹²¹, R¹²², R¹²³, R¹²⁴, R¹²⁵, R¹²⁶, R¹²⁷: each independently may represent alkyl, aryl group; -C_nH_{2n}SO₃M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C_nH_{2n}COOR¹³¹ (n represents an integer from 1 to 5 and R¹³¹ alkyl, or aryl group); -L¹-CONHSO₂R¹³² (L¹ represents -C_nH_{2n}- with n an integer from 1 to 4 and R¹³² alkyl or aryl). R¹²⁰ together with R¹²¹, R¹²² together with R¹²³, R¹²⁴ together with R¹²⁵, R¹²⁶ together with R¹²⁷ may form a cyclic ring. R¹²⁸, R¹²⁹, R¹³⁰: each independently may represent hydrogen, alkyl, or aryl group; R¹²⁹ may represent halogen, ester, or -SO₂R¹³³ (R¹³³ represents alkyl, or aryl).

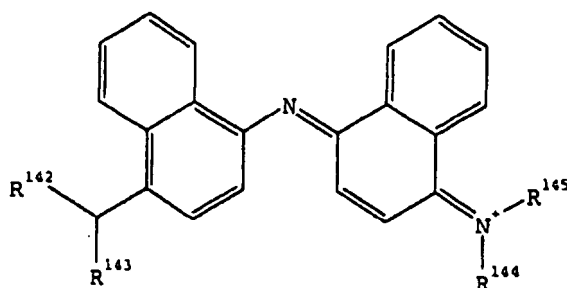


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R¹³⁴, R¹³⁷, R¹³⁸, R¹⁴¹ each independently may represent: hydrogen, alkyl, or aryl
 R¹³⁴ together with R¹³⁵, R¹⁴¹ together with R¹⁴⁰ may form a carbocyclic ring.
 R¹³⁵ together with R¹³⁶, R¹³⁹ together with R¹⁴⁰ may form a carbocyclic ring.
 R¹³⁵, R¹³⁶, R¹³⁹, R¹⁴⁰ each independently may represent: hydrogen, alkyl, aryl group; -C_nH_{2n}SO₃M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion);

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R¹⁴², R¹⁴³, R¹⁴⁴, R¹⁴⁵ each independently represents alkyl, aryl group; -C_nH_{2n}SO₃M represents an integer from 2 to 4 and M H or positively charged counterion); -C_nH_{2n}COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C_nH_{2n}COOR¹⁴⁶ (n represents an integer from 1 to 5 and R¹⁴⁶ alkyl, or aryl group); -L1-CONHSO₂R¹⁴⁷ (L1 represents -C_nH_{2n}- with n an integer from 1 to 4 and R¹⁴⁷ alkyl or aryl). R¹⁴² together with R¹⁴³, R¹⁴⁴ together with R¹⁴⁵ may form a cyclic ring.

The charge of the dyes can be compensated by any (intermolecular or intramolecular) counterion.

[0039] The IR-dyes are present preferably in an amount between 1 and 60 parts, more preferably between 3 and 50 parts by weight of the total amount of said IR-sensitive top layer.

[0040] The alkali soluble polymers used in this layer are preferably hydrophobic and ink accepting polymers as used in conventional positive or negative working PS-plates e.g. carboxy substituted polymers etc. More preferably is a phenolic resin such as polyvinylphenol or a novolac polymer. Most preferred is a novolac polymer. Typical examples of these polymers are described in DE-A- 4 007 428, DE-A-4 4 027 301 and DE-A- 4 445 820. The hydrophobic polymer used in connection with the present invention is further characterised by insolubility in water and at least partial solubility/swellability in an alkaline solution and/or at least partial solubility in water when combined with a cosolvent.

[0041] Furthermore this IR-sensitive layer is preferably a visible light- and UV-light desensitised layer. Still further said layer is preferably thermally hardenable. This preferably visible light- or UV-light desensitised layer does not comprise photosensitive ingredients such as diazo compounds, photoacids, photoinitiators, quinone diazides, sensitisers etc. which absorb in the wavelength range of 250nm to 650nm. In this way a daylight stable printing plate can be obtained.

[0042] Said IR-sensitive layer preferably also includes a low molecular acid, more preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid or a benzophenone, more preferably trihydroxybenzophenone.

[0043] The ratio between the total amount of low molecular acid or benzophenone and polymer in the IR-sensitive layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 30:70. The total amount of said IR-sensitive layer preferably ranges from 0.1 to 10 g/m², more preferably from 0.3 to 2 g/m².

[0044] In the IR-sensitive layer a difference in the capacity of being penetrated and/or solubilised by the alkaline developer containing SiO₂ and M₂O in a molar ratio of 0.5 to 1.5 and a concentration of SiO₂ of 0.5 to 5% by weight is generated upon image-wise exposure for an alkaline developer according to the invention.

[0045] In the imaging element according to the present invention, the lithographic base is an electrochemically grained and anodised aluminum support which has been treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB-A-1 084 070, DE-A-4 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A-537 633, DE-A- 4 001466, EP-A-292 801, EP-A-291 760 and US-P- 4 458 005.

[0046] Image-wise exposure in connection with the present invention is an image-wise scanning exposure involving the use of a laser that operates in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared. Exposure of the imaging element can be performed with lasers with a short as well as with lasers with a long pixel dwell time. Preferred are lasers with a pixel dwell time between 0.005 μs and 20 μs.

[0047] After the image-wise exposure the heat mode imaging element is developed by rinsing it with an aqueous alkaline solution. The aqueous alkaline solutions used in the present invention are those that are used for developing conventional positive working presensitized printing plates and have preferably a pH between 11.5 and 14. Thus the imaged parts of the top layer that were rendered more penetrable for the aqueous alkaline solution upon exposure are cleaned-out whereby a positive working printing plate is obtained.

[0048] In the present invention, the composition of the developer used is also very important.

[0049] Therefore, to perform development processing stably for a long time period particularly important are qualities such as strength of alkali and the concentration of silicates in the developer. Under such circumstances, the present inventors have found that a rapid high temperature processing can be performed, that the amount of the replenisher to be supplemented is low and that a stable development processing can be performed over a long time period of the order of not less than 3 months without exchanging the developer only when the developer having the foregoing composition is used.

[0050] The developers and replenishers for developer used in the invention are preferably aqueous solutions mainly composed of alkali metal silicates and alkali metal hydroxides represented by MOH or their oxide, represented by M_2O , wherein said developer comprises SiO_2 and M_2O in a molar ratio of 0.5 to 1.5. As such alkali metal silicates, preferably used are, for instance, sodium silicate, potassium silicate, lithium silicate and sodium metasilicate. On the other hand, as such alkali metal hydroxides, preferred are sodium hydroxide, potassium hydroxide and lithium hydroxide.

[0051] The developers used in the invention may simultaneously contain other alkaline agents. Examples of such other alkaline agents include such inorganic alkaline agents as ammonium hydroxide, sodium tertiary phosphate, sodium secondary phosphate, potassium tertiary phosphate, potassium secondary phosphate, ammonium tertiary phosphate, ammonium secondary phosphate, sodium bicarbonate, sodium carbonate, potassium carbonate and ammonium carbonate; and such organic alkaline agents as mono-, di- or triethanolamine, mono-, di- or trimethylamine, mono-, di- or triethylamine, mono- or diisopropylamine, n-butylamine, mono-, di- or triisopropanolamine, ethyleneimine, ethylenediamine and tetramethylammonium hydroxide.

[0052] In the present invention, particularly important is the molar ratio in the developer of $[SiO_2] / [M_2O]$, which is generally 0.6 to 1.5, preferably 0.7 to 1.3. This is because if the molar ratio is less than 0.6, great scattering of activity is observed, while if it exceeds 1.5, it becomes difficult to perform rapid development and the dissolving out or removal of the light-sensitive layer on non-image areas is liable to be incomplete. In addition, the concentration of SiO_2 in the developer and replenisher preferably ranges from 1 to 4 % by weight. Such limitation of the concentration of SiO_2 makes it possible to stably provide lithographic printing plates having good finishing qualities even when a large amount of plates according to the invention are processed for a long time period.

[0053] In a particular preferred embodiment, an aqueous solution of an alkali metal silicate having a molar ratio $[SiO_2] / [M_2O]$, which ranges from 1.0 to 1.5 and a concentration of SiO_2 of 1 to 4 % by weight is used as a developer. In such case, it is a matter of course that a replenisher having alkali strength equal to or more than that of the developer is employed. In order to decrease the amount of the replenisher to be supplied, it is advantageous that a molar ratio, $[SiO_2] / [M_2O]$, of the replenisher is equal to or smaller than that of the developer, or that a concentration of SiO_2 is high if the molar ratio of the developer is equal to that of the replenisher.

[0054] In the developers and the replenishers used in the invention, it is possible to simultaneously use organic solvents having solubility in water at 20 °C of not more than 10 % by weight according to need. Examples of such organic solvents are such carboxylic acid esters as ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, ethylene glycol monobutyl acetate, butyl lactate and butyl levulinate; such ketones as ethyl butyl ketone, methyl isobutyl ketone and cyclohexanone; such alcohols as ethylene glycol monobutyl ether, ethylene glycol benzyl ether, ethylene glycol monophenyl ether, benzyl alcohol, methylphenylcarbinol, n-amyl alcohol and methylamyl alcohol; such alkyl-substituted aromatic hydrocarbons as xylene; and such halogenated hydrocarbons as methylene dichloride and monochlorobenzene. These organic solvents may be used alone or in combination. Particularly preferred is benzyl alcohol in the invention. These organic solvents are added to the developer or replenisher therefor generally in an amount of not more than 5 % by weight and preferably not more than 4 % by weight.

[0055] The developers and replenishers used in the present invention may simultaneously contain a surfactant for the purpose of improving developing properties thereof. Examples of such surfactants include salts of higher alcohol (C8 - C22) sulfuric acid esters such as sodium salt of lauryl alcohol sulfate, sodium salt of octyl alcohol sulfate, ammonium salt of lauryl alcohol sulfate. Teepol B-81 (trade mark, available from Shell Chemicals Co., Ltd.) and disodium alkyl sulfates; salts of aliphatic alcohol phosphoric acid esters such as sodium salt of cetyl alcohol phosphate; alkyl aryl sulfonic acid salts such as sodium salt of dodecylbenzene sulfonate, sodium salt of isopropyl naphthalene sulfonate, sodium salt of dinaphthalene disulfonate and sodium salt of metanilrobenzene sulfonate; sulfonic acid salts of alkylamides such as $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$ and sulfonic acid salts of dibasic aliphatic acid esters such as sodium dioctyl sulfosuccinate and sodium dihexyl sulfosuccinate. These surfactants may be used alone or in combination. Particularly preferred are sulfonic acid salts. These surfactants may be used in an amount of generally not more than 5 % by weight and preferably not more than 3 % by weight.

[0056] The developer used in the method of the present invention comprises as anionic or amphoteric surfactant such as sodium alkyl naphthalene sulfonate and N-tetradecyl-N,N-dihydroxyethyl betaine as disclosed in JN-A- 50-51324. In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0057] Examples of such compounds are neutral salts such as NaCl, KCl and KBr as disclosed in **JN-A- 58- 75 152**; chelating agents such as EDTA and NTA as disclosed in **JN-A- 58- 190 952** (U.S-A- 4 469 776), complexes such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as disclosed in **JN-A- 59-121 338** (US-A-4 608 995); ionizable compounds of elements of the group IIa, IIIa or IIIb of the Periodic Table such as those disclosed in **JN-A- 55- 25 100**; tetramethyldecyne diol as disclosed in US-A-4 4 374 920; non-ionic surfactants as disclosed in **JN-A- 60-213 943**; cationic polymers such as methyl chloride quaternary products of p-dimethylaminomethyl polystyrene as disclosed in **JN-A- 55- 95 946**; amphoteric polyelectrolytes such as copolymer of vinylbenzyl trimethylammonium chloride and sodium acrylate as disclosed in **JN-A- 58-142 528**; reducing inorganic salts such as sodium sulfite as disclosed in **JN-A- 57-192 952** (US-A- 467 027) and alkaline-soluble mercapto compounds or thioether compounds such as thioisocyclic acid, cysteine and thioglycolic acid; inorganic lithium compounds such as lithium chloride as disclosed in **JN-A-58- 59 444**; organic lithium compounds such as lithium benzoate as disclosed in **JN-A- 50-34 442**; organometallic surfactants containing Si, Ti or the like as disclosed in **JN-A- 59- 75 255**; organoboron compounds as disclosed in **JN-A- 59- 84 241** (US-A-4 500 625); quaternary ammonium salts such as tetraalkylammonium oxides as disclosed in EP-A-101 010; and bactericides such as sodium dehydroacetate as disclosed in **JN-A- 63- 226 657**. In the method for development processing of the present invention, any known means of supplementing a replenisher for developer may be employed. Examples of such methods preferably used are a method for intermittently or continuously supplementing a replenisher as a function of the amount of PS plates processed and time as disclosed in **JN-A-55-115 039** (GB-A- 2 046 931), a method comprising disposing a sensor for detecting the degree of light-sensitive layer dissolved out in the middle portion of a developing zone and supplementing the replenisher in proportion to the detected degree of the light-sensitive layer dissolved out as disclosed in **JN-A- 58- 95 349** (US-A- 4 537 496); a method comprising determining the impedance value of a developer and processing the detected impedance value by a computer to perform supplementation of a replenisher as disclosed in GB-A- 2 208 249.

[0058] The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slid on the print cylinder instead of applying in a classical way a classically formed printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

[0059] After the development of an image-wise exposed imaging element with an aqueous alkaline solution and drying, the obtained plate can be used as a printing plate as such. However, to improve durability it is still possible to bake said plate at a temperature between 200°C and 300°C for a period of 30 seconds to 5 minutes. Also the imaging element can be subjected to an overall post-exposure to UV-radiation to harden the image in order to increase the run length of the printing plate.

[0060] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

EXAMPLE

EXAMPLE 1 :Positive working thermal plate based on an alkali-soluble binder.

Preparation of the lithographic base

[0061] A 0.20 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m² to form a surface topography with an average center-line roughness Ra of 0.5 mm.

[0062] After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

[0063] The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m² for about 300 seconds to form an anodic oxidation film of 3.00 g/m² of Al₂O₃ then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and then with a solution containing aluminum trichloride, subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the IR-sensitive layer.

[0064] The IR-sensitive layer was coated from a 4.65 % wt solution in tetrahydrofuran/methoxypropanol 60/40 at a wet thickness of 30 μm. The resulting IR-sensitive layer contained 10% of IR-dye compound I and 90% of ALNOVOL PN430™.

[0065] This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 4 W. After IR-exposure no layer damage, as a result of ablation, could be observed.

After exposure the material was developed in an alkaline developing solution (EP 240 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

EXAMPLE 2 Positive working thermal plate based on an alkali-soluble binder.

[0066] The lithographic base was prepared as described in example 1.

[0067] The IR-sensitive layer was coated from a 4.65 % wt solution in tetrahydrofuran/methoxypropanol 60/40 at a wet thickness of 30 μm. The resulting IR-sensitive layer contained 4.7% of IR-dye compound II, 78.1% of ALNOVOL PN430™ and 17.2 % of trihydroxybenzophenone.

[0068] This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 4 W. After IR-exposure no layer damage, as a result of ablation, could be observed. After exposure the material was developed in an alkaline developing solution (EP 26 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

[0069] The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

EXAMPLE 3 :Positive working thermal plate based on an alkali-soluble binder.

[0070] The lithographic base was prepared as described in example 1.

[0071] The IR-sensitive layer was coated from a 4.65 % wt solution in tetrahydrofuran/methoxypropanol 60/40 at a wet thickness of 30 μm. The resulting IR-sensitive layer contained 9.1% of IR-dye compound II, 74.5% of ALNOVOL PN430™ and 16.4 % of trihydroxybenzophenone.

[0072] This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 4 W. After IR-exposure no layer damage, as a result of ablation, could be observed.

After exposure the material was developed in an alkaline developing solution (EP 26 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

Claims

1. A method for making lithographic printing plates including the following steps

a) preparing a heat mode imaging element consisting of (i) an electrochemically grained and anodised aluminum

support which has been treated to improve the hydrophilic properties of its surface by a step selected from :

- treating the aluminum oxide surface with a sodium silicate solution at elevated temperature, or
- treating the aluminum oxide surface with a phosphate solution, or
- rinsing the aluminum oxide surface with a citric acid solution, a citrate solution or a bicarbonate solution, or
- treating the aluminum oxide surface with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde,

and (ii) a top layer which does not contain a photoacid, and which is sensitive to IR-radiation and which comprises a polymer, soluble in an aqueous alkaline solution, and which is unpenetrable for an alkaline developer containing SiO₂ and M₂O in a molar ratio of 0.5 to 1.5 and a concentration of SiO₂ of 0.5 to 5% by weight;

- 5
- b) exposing imagewise said heat mode imaging element to IR-radiation;
 c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer are dissolved and the unexposed areas of the top layer remain undissolved,

10 wherein said top layer includes an IR-dye selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphenyl and triphenyl azo compounds and squarylium derivatives, and wherein said developer further comprises an anionic or amphoteric surfactant.

- 15 **2.** A method for making lithographic printing plates according to claim 1 wherein said polymer included in the IR-sensitive layer is a hydrophobic polymer.
- 3.** A method for making lithographic printing plates according to any of claims 1 or 2 wherein said IR-sensitive layer is a visible light- and UV light-desensitized layer.
- 20 **4.** A method for making lithographic printing plates according to any of claims 1 to 3 wherein said IR-sensitive layer is thermally hardenable.

25 **Patentansprüche**

- 1.** Ein Verfahren zur Herstellung lithografischer Druckplatten, das folgende Schritte umfasst :

a) Herstellung eines wärmeempfindlichen bilderzeugenden Elements, bestehend aus :

30 (i) einem elektrochemisch angerauten und anodisierten Aluminiumträger, dessen Oberfläche zur Verbesserung ihrer hydrophilen Eigenschaften durch einen der folgenden Schritte verarbeitet worden ist :

- 35 - Verarbeitung der Aluminiumoxidoberfläche mit einer Natriumsilikatlösung bei erhöhter Temperatur oder
 - Verarbeitung der Aluminiumoxidoberfläche mit einer Phosphatlösung oder
 - Spülung der Aluminiumoxidoberfläche mit einer Zitronensäurelösung, einer Citratlösung oder einer Bicarbonatlösung, oder
 40 - Verarbeitung der Aluminiumoxidoberfläche mit Polyvinylphosphonsäure, Polyvinylmethylphosphonsäure, Phosphorsäureestern von Polyvinylalkohol, Polyvinylsulfonsäure, Polyvinylbenzolsulfonsäure, Schwefelsäureestern von Polyvinylalkohol und Acetalen von Polyvinylalkoholen, die durch Reaktion mit einem sulfonierten alifatischen Aldehyd gebildet sind,

45 und (ii) einer Deckschicht, die keine Fotosäure enthält, empfindlich gegenüber Infrarotstrahlung ist, ein in einer wässrig-alkalischen Lösung lösliches Polymer enthält und undurchdringlich für einen alkalischen, SiO₂ und M₂O in einem Molverhältnis von 0,5 bis 1,5 und einem SiO₂-Gewichtsverhältnis von 0,5 bis 5 Gew.-% enthaltenden Entwickler ist,

- 50 b) bildmäßige Belichtung des wärmeempfindlichen bilderzeugenden Elements mit Infrarotstrahlung,
 c) Entwicklung des bildmäßig belichteten wärmeempfindlichen bilderzeugenden Elements mit dem alkalischen Entwickler, so dass die belichteten Bereiche der Deckschicht gelöst werden und die nicht-belichteten Bereiche der Deckschicht ungelöst bleiben,

55 **dadurch gekennzeichnet, dass** die Deckschicht einen Infrarot-Farbstoff aus der Gruppe bestehend aus Indoanilinfarbstoffen, Cyaninfarbstoffen, Merocyaninfarbstoffen, Oxonolfarbstoffen, Porphin-Derivaten, Anthrachinonfarbstoffen, Merostyrylfarbstoffen, Pyryliumverbindungen, Diphenylverbindungen, Triphenylazoverbindungen und Squarylium-Derivaten enthält, **und dadurch gekennzeichnet, dass** der Entwickler ferner ein anionisches oder amfoteres Tensid enthält.

2. Verfahren zur Herstellung lithografischer Druckplatten nach Anspruch 1, **dadurch gekennzeichnet, dass** das in der gegenüber Infrarotstrahlung empfindlichen Schicht enthaltene Polymer ein hydrophobes Polymer ist.
3. Verfahren zur Herstellung lithografischer Druckplatten nach einem der Ansprüche 1 oder 2, **dadurch gekennzeichnet, dass** die gegenüber Infrarotstrahlung empfindliche Schicht eine gegenüber sichtbarem Licht und Ultraviolettlicht unempfindlich gemachte Schicht ist.
4. Verfahren zur Herstellung lithografischer Druckplatten nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die gegenüber Infrarotstrahlung empfindliche Schicht wärmehärtend ist.

Revendications

1. Un procédé pour la confection de plaques d'impression lithographiques, comprenant les étapes ci-après :

a) la confection d'un élément formateur d'image thermosensible composé

(i) d'un support aluminium grainé électrochimiquement et anodisé dont les propriétés hydrophiles ont été améliorées en ayant soumis sa surface à l'un des traitements ci-après :

- le traitement de la surface d'oxyde d'aluminium avec une solution de silicate de sodium à température élevée, ou

- le traitement de la surface d'oxyde d'aluminium avec une solution de phosphate, ou

- le rinçage de la surface d'oxyde d'aluminium avec une solution d'acide citrique, une solution de citrate ou une solution de bicarbonate, ou

- le traitement de la surface d'oxyde d'aluminium avec de l'acide polyvinylphosphonique, de l'acide polyvinylméthylphosphonique, des esters de l'acide phosphorique d'alcool polyvinylique, de l'acide polyvinylsulfonique, de l'acide polyvinylbenzènesulfonique, des esters de l'acide sulfurique d'alcool polyvinylique et des acétals d'alcools polyvinyliques formés par réaction avec un aldéhyde aliphatique sulfoné,

et (ii) d'une couche superficielle qui ne contient pas de photoacide, qui est sensible aux rayons infrarouges, qui contient un polymère soluble dans une solution alcaline aqueuse et qui est impénétrable pour un révélateur alcalin contenant du SiO_2 et du M_2O dans un rapport molaire de 0,5 à 1,5 et dans un rapport pondéral de SiO_2 compris entre 0,5 et 5% en poids,

b) l'exposition sous forme d'image aux rayons infrarouges de l'élément formateur d'image thermosensible,

c) le développement de l'élément formateur d'image thermosensible exposé sous forme d'image en utilisant ledit révélateur alcalin de façon à ce que les zones exposées de la couche superficielle soient dissoutes et que les zones non exposées de la couche superficielle restent intactes,

caractérisé en ce que la couche superficielle contient un colorant absorbant les rayons infrarouges choisi parmi le groupe composé de colorants d'indoaniline, de colorants de cyanine, de colorants de mérocyanine, de colorants d'oxonol, de dérivés de porphine, de colorants d'antraquinone, de colorants mérostyryliques, de composés de pyrilium, de composés de diphenyle, de composés triphénylazoïques et de dérivés de squarylium, et **caractérisé en ce que** le révélateur contient en outre un agent tensioactif anionique ou amphotère.

2. Procédé pour la confection de plaques d'impression lithographiques selon la revendication 1, **caractérisé en ce que** le polymère contenu dans la couche sensible aux rayons infrarouges est un polymère hydrophobe.
3. Procédé pour la confection de plaques d'impression lithographiques selon l'une quelconque des revendications 1 ou 2, **caractérisé en ce que** la couche sensible aux rayons infrarouges est désensibilisée à la lumière visible et à la lumière ultraviolette.
4. Procédé pour la confection de plaques d'impression lithographiques selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** la couche sensible aux rayons infrarouges est une couche thermodurcissable.

REFERENCES CITED IN THE DESCRIPTION

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