(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 943 451 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
05.06.2002 Bulletin 2002/23

(51) Int Cl.[7]: **B41M 5/36**, B41C 1/10

(21) Application number: **99200336.8**

(22) Date of filing: **05.02.1999**

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

Ein wärmeempfindliches Bildaufzeichnungsmaterial und ein Verfahren zur Herstellung einer positiv arbeitenden Druckplatte aus demselben wärmeempfindlichen Material

Elément pour l'enregistrement de l'image thermosensible et le procédé pour la fabrication d'une plaque d'impression positive à partir de cet élément

(84) Designated Contracting States:
BE DE FR GB

(30) Priority: **14.03.1998 EP 98200831**

(43) Date of publication of application:
22.09.1999 Bulletin 1999/38

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EP-A- 0 573 092
EP-A- 0 823 327
FR-A- 1 561 957
GB-A- 1 154 568
GB-A- 1 155 035
GB-A- 1 160 221
GB-A- 1 208 415
GB-A- 1 245 924
US-A- 5 466 557
US-A- 5 641 608

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Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a heat mode imaging element for preparing a lithographic printing plate comprising an IR sensitive top layer.
More specifically the invention is related to a heat mode imaging element for preparing a lithographic printing plate with a higher sensitivity.

BACKGROUND OF THE INVENTION

[0002] Lithography is the process of printing from specially 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.
[0003] 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.
[0004] 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 diazo-sensitized systems are widely used.
[0005] 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.
[0006] 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.
[0007] 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.
[0008] 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. Therefor it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide may 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.
[0009] **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.
[0010] 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.
[0011] 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, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.
[0012] **US-P- 4 708 925** discloses imaging elements including a photosensitive composition comprising an alkali-

soluble novolac resin and an onium-salt. This composition may 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.

[0013] **EP-A- 625 728** discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which may 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.

[0014] **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.

[0015] 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.

[0016] **EP-A- 573 092** discloses a method for making an image comprising the steps of:

- image-wise exposing a heat mode recording material containing on a support (i) a recording layer containing a radiation to heat converting substance and an image forming substance and optionally (ii) a surface layer thereby
- decomposing said recording layer and optionally said surface layer in the exposed areas and
- rubbing said heat mode recording material to remove said optional surface layer and said recording layer in the exposed areas. Said material is not developed with a developing solution.

[0017] **EP-A- 823 327** discloses a positive photosensitive composition showing a difference in solubility in alkali developer as between an exposed portion and a non-exposed portion, which comprises as components inducing the difference in solubility ,

(a) a photo-thermal conversion material, and
(b) a high molecular compound, of which the solubility in an alkali developer is changeable mainly by a change other than a chemical change.

[0018] **FR-A- 1 561 957** discloses a process in order of registering or reproducing information by means of electromagnetic radiation and also discloses elements sensible for heat containing substances wherein heat is produced by exposure to electromagnetic radiation.

[0019] **US-A- 5 641 608** discloses a process for the direct production of an imaged pattern of resist on a substrate, which process utilizes thermo-resist rather than photoresist, i.e. compositions which undergo thermally-induced, rather than photo-induced, chemical transformations. A film of thermo-resist composition applied to the surface substrate is scanned by a focused heat source in a predetermined pattern, without a phototool, to bring about localized thermally-induced chemical transformations of the composition which either directly produce the resist pattern or produce in the film a developable latent image of the pattern.

[0020] **GB-A- 1 208 415** discloses a method of recording information comprising information-wise heating a recording material comprising a support bearing, with or without an inter-layer, a heat-sensitive recording layer constituted so that such information-wise heating creates a record of the information in terms of a difference in the water-permeability of different areas of the recording layer, treating the recording material with an aqueous liquid which penetrates through the water-permeable or more water permeable areas of the recrding layer and is constituted so as to effect a permanent physical and/or chemical change of at least the surface portions of the underlying support or inter-layer in the corresponding areas, and removing the whole of the recording layer to expose said information-wise changed underlying support or inter-layer.

[0021] **US-A- 5 466 557** discloses a radiation sensitive composition especially adapted to prepare a lithographic printing plate that is sensitive to both ultraviolet and infrared radiation and capable of functioning in either a positive-working or negative-working manner, comprised of (1) a resole resin, (2) a novolac resin, (3) a latent Bronsted acid, (4) an infrared absorber, and (5) terephthalaldehyde. The solubility of the composition in aqueous alkaline developing solution is both reduced in exposed areas and increased in unexposed areas by the steps of imagewise exposure to activating radiation and heating.

[0022] **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 soluble or most soluble in such solvent to be removed or penetrated by such solvent, the said method being characterized in that the said recording layer is wholly or mainly composed of one or more heat-sensitive polymeric compounds.

[0023] **GB-A- 1 155 035** 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 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.

[0024] **EP-A- 97 200 588.8** discloses a heat mode imaging element for making lithographic printing plates comprising on a lithographic base having a hydrophilic surface an intermediate layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation wherein said top layer upon exposure to IR-radiation has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution.

[0025] Said last heat-mode imaging element has the disadvantage that the sensitivity is marginal. An analogous material with a higher IR-sensitivity would be appreciated.

OBJECTS OF THE INVENTION

[0026] It is an object of the invention to provide a heat mode imaging elements for making lithographic printing plates in an easy way

[0027] It is an object of the invention to provide a heat mode sensitive imaging element for making positive lithographic printing plates having excellent printing properties, developable in a selective, rapid convenient and ecological way.

[0028] It is further an object of the present invention to provide a heat mode sensitive imaging element for making positive lithographic printing plates wherein said heat mode sensitive imaging element has a high infrared sensitivity.

[0029] Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION

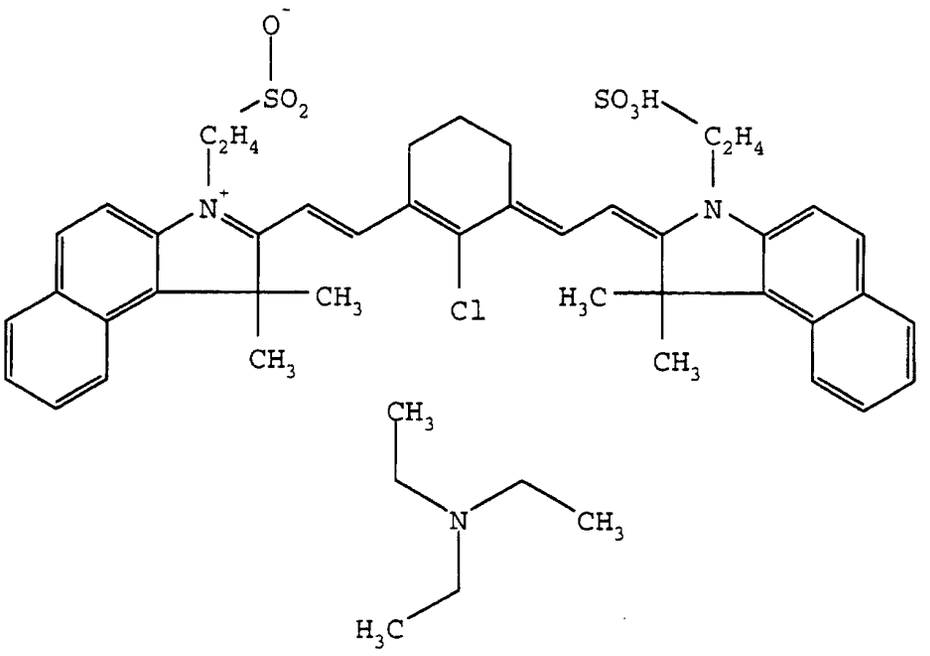
[0030] According to the present invention there is provided a heat mode imaging element for making a lithographic printing plate having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is unpenetrable for or insoluble in an alkaline developer containing SiO_2 in the form of silicates before imagewise IR exposure, imaged parts being capable of removal during development without solubilising and/or damaging non-imaged parts; characterized in that said first layer and said top layer comprise a compound capable of converting IR-light into heat. Also provided is a method of making alithographic printing plate according to claim 10.

DETAILED DESCRIPTION OF THE INVENTION

[0031] It has been found that a heat-sensitive imaging element according to the invention has a high sensitivity and yields a lithographic printing plate of high quality.

[0032] The first layer and the top (also called the second) layer comprise a compound capable of converting IR-light into heat. Said compound capable of converting IR-light into heat is preferably an IR dye or pigment. A mixture of IR-dyes or pigments may be used, but it is preferred to use only one IR-dye or pigment.

[0033] Preferably said IR-dyes are IR-cyanines dyes. Particularly useful IR-cyanine dyes are cyanines dyes with at least two acid groups, more preferably with at least two sulphonic groups . Still more preferably are cyanines dyes with two indolenine and at least two sulphonic acid groups. Most preferably is compound I with the structure as indicated



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Particularly useful IR-absorbing pigments are carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. W02.9. It is also possible to use conductive polymer dispersion such as polypyrrole or polyaniline-based conductive polymer dispersions. The lithographic performance and in particular the print endurance obtained depends on the heat-sensitivity of the imaging element. In this respect it has been found that carbon black yields very good and favorable results.

[0034] The top layer, in accordance with the present invention comprises a compound capable of converting IR-light into heat, preferably an IR-dye or pigment as set out above and preferably a binder resin.

[0035] The compound capable of converting IR-light into heat is present in said top layer preferably in an amount between 1 and 99 parts, more preferably between 50 and 95 parts by weight of the total weight of said IR-sensitive top layer.

[0036] The top layer may preferably comprise as binder a water insoluble polymer, more preferably an alkaline insoluble polymer such as a cellulose ester, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, silicone resins, etc. Preferred as binder is nitrocellulose resin.

[0037] The total amount of the top layer preferably ranges from 0.1 to 10 g/m^2, more preferably from 0.3 to 2 g/m^2.

[0038] In the top layer a difference in the capacity of being penetrated and/or solubilised by the aqueous alkaline solution is generated upon image-wise exposure according to the invention.

[0039] In the present invention the said capacity is increased upon image-wise IR exposure to such degree that the imaged parts will be cleaned out during development without solubilising and/or damaging the non-imaged parts.

[0040] The development with the aqueous alkaline solution is preferably done within an interval of 5 to 120 seconds.

[0041] Between the top layer and the lithographic base the present invention comprises a first layer soluble in an aqueous developing solution, more preferably an aqueous alkaline developing solution with preferentially a pH between 7.5 and 14. Said layer is preferably contiguous to the top layer but other layers may be present between the top layer and the first layer. Said layer comprise a compound capable of converting IR-light into heat, preferably an IR dye or pigment and an alkali soluble binder. Said compound capable of converting IR-light into heat is present in said first layer in an amount of 0.1 to 30 parts, more preferably in an amount between 1 and 20 parts by weight of the total weight of said first layer. Said compound capable of converting IR-light into heat preferably does not decrease the solubility of the first layer in aqueous alkaline solution.

[0042] The alkali soluble binders used in this layer are preferably hydrophobic binders as used in conventional positive or negative working PS-plates e.g. novolac resins, polymers containing hydroxystyrene units, carboxy substituted polymers etc. Typical examples of these polymers are descibed in **DE-A- 4 007 428, DE-A- 4 027 301** and **DE-A- 4 445 820**. The hydrophobic binder used in connection with the present invention is further characterised by insolubility in water and in an alkaline solution and/or partial solubility in water when combined with a cosolvent.

[0043] Furthermore this aqueous alkali soluble layer is preferably a visible light- and UV-light desensitised layer. Said layer is preferably thermally hardenable. This preferably visible light- and UV-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 may be obtained.

[0044] Said first layer preferably also includes a low molecular acid, preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid or a benzophenone.

[0045] The ratio between the total amount of low molecular acid or benzophenone and polymer in the first layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 20:80. The total amount of said first layer preferably ranges from 0.1 to 10 g/m^2, more preferably from 0.3 to 2 g/m^2.

[0046] In the imaging element according to the present invention, the lithographic base may be an anodised aluminum. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be 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 may 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- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760** and **US-P- 4 458 005.**

[0047] According to another mode in connection with the present invention, the lithographic base having a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetraalkylorthosilicate. The latter is particularly preferred.

[0048] As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

[0049] The amount of crosslinking agent, in particular of tetraalkyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, more preferably between 0.5 and 5 parts by weight, most preferably between 1.0 parts by weight and 3 parts by weight.

[0050] A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica may be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

[0051] The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 μm and is preferably 1 to 10 μm.

[0052] Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in **EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, US-P- 4 284 705** and **EP-A- 514 490.**

[0053] As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent.

[0054] It is particularly preferred to use a polyester film support to which an adhesion improving layer has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in **EP-A- 619 524, EP-A- 620 502** and **EP-A- 619 525.** Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

[0055] 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 may 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.

[0056] After the image-wise exposure the heat mode imaging element is developed by rinsing it with an aqueous alkaline solution containing SiO_2 in the form of silicates . The aqueous alkaline solutions used in the present invention are those that are used for developing conventional positive working presensitised 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.

[0057] In the present invention, the composition of the developer used is also very important.

[0058] 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.

[0059] 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 oxyde, represented by M_2O, wherein said developer comprises SiO_2.of 0.5 to 1.5 and a concentration of SiO_2 of 0.5 to 5% by weight. 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.

[0060] 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, ethylenediimine and tetramethylammonium hydroxide.

[0061] 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.

[0062] 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.

[0063] 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 carboxilic 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.

[0064] 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 isopropylnaphthalene sulfonate, sodium salt of dinaphthalene disulfonate and sodium salt of metanitrobenzene 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.

[0065] In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0066] 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 [Co(NH3)6]Cl3 as disclosed in **JN-A- 59- 121 336 (US-A- 4 606 995);** 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;** anionic or amphoteric surfactants such as sodium alkyl naphthalene sulfonate and N-tetradecyl-N,N-dihydroxythyl betaine as disclosed in **JN-A- 50- 51 324;** tetramethyldecyne diol as disclosed in **US-A- 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- 56- 142 528;** reducing inorganic salts such as sodium sulfite as disclosed in **JN-A- 57- 192 952 (US-A- 4 467 027)** and alkaline-soluble mercapto compounds or thioether compounds such as thiosalicylic 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.**

[0067] 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.**

[0068] 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 slided 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.

[0069] 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 lenght of the printing plate.

[0070] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

Example 1 (comparative): Material with no IR-absorbing compound in the first layer

[0071]

- Preparation of the lithographic base

  A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l cf 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/m^2 to form a surface topography with an average center-line roughness Ra of 0.5 mm.

  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.

  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/m^2 for about 300 seconds

to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3 then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and washed with demineralized water at 20°C during 120 seconds and dried.

- The first layer was coated from THF/2-methoxypropanol (in a ratio of 55/45) at a wet thickness of 14 μm resulting in a dry coating weight of 1.10 g/m^2. This resulted in the following dry composition: 0.970 g/m^2 of Alnovol SPN452 (cresol novolac from Hoechst) and 0.130 g/m^2 of 3,4,5-trimethoxybenzoic acid (available from Aldrich).

- The top layer was coated from MEK/Dowanol in a ratio of 50/50 at a wet thickness of 20 μm resulting in a dry coating weight of 0.146 g/m^2. This resulted in the following dry coating composition : 0.115 g/m^2 of Special Schwarz 250 (carbon black available from Degussa), 0.003 g/m^2 of Solsperse 5000 (dispersing agent available fron ICI), 0.011 g/m^2 of Solsperse 28000 (dispersing agent available from ICI), 0.011 g/m^2 of Nitrocellulose E950 (available from Wolff Walsrode), 0.005 g/m^2 of Tego Glide 410 (dispersing agent available from Tego Chemie Service GmbH) and 0.002 g/m^2 of Tego Wet 265 (dispersing agent available from Tego Chemie Service GmbH).

Example 2 : Material with 2.5 % w/w carbon black as IR-absorbing compound in the first layer.

[0072]

- The first layer was coated on a lithographic base as described in example 1 from THF/2-methoxypropanol (in a ratio of 55/45) at a wet thickness of 14 μm resulting in a dry coating weight of 1.10 g/m^2. This resulted in the following dry composition : 0.780 g/m^2 of Alnovol SPN452 (novolac from Hoechst), 0.133 g/m^2 of 3,4,5-trimethoxybenzoic acid (available from Aldrich), 0.027 g/m^2 of Printex G (carbon black available from Degussa) and 0.160 g/m^2 of Alnovol SPN400 (novolac from Hoechst).

- The same top layer as described in example 1 was used for this example.

Example 3 : Material with 5 % w/w carbon black as IR-absorbing compound in the first layer.

[0073] The first layer was coated on a lithographic base as described in example 1 from THF/2-methoxypropanol (in a ratio of 55/45) at a wet thickness of 14 μm resulting in a dry coating weight of 1.10 g/m^2. This resulted in the following dry composition : 0.569 g/m^2 of Alnovol SPN452 (novolac from Hoechst), 0.133 g/m^2 of 3,4,5-trimethoxybenzoic acid (available from Aldrich), 0.053 g/m^2 of Printex G (carbon black available from Degussa) and 0.345 g/m^2 of Alnovol SPN400 (novolac from Hoechst).

- The same top layer as described in example 1 was used for this example.

Example 4 (comparative): Material with an increased concentration of carbon black in the top layer.

[0074]

- The first layer was coated on a lithographic base as described in example 1 from THF/2-methoxypropanol (in a ratio of 55/45) at a wet thickness of 14 μm resulting in a dry coating weight of 1.10 g/m^2. This resulted in the following dry composition : 0.970 g/m^2 of Alnovol SPN452 (cresol novolac from Hoechst) and 0.130 g/m^2 of 3,4,5-trimethoxybenzoic acid (available from Aldrich).

- The top layer was coated from MEK/Dowanol in a ratio of 50/50 at a wet thickness of 20 μm resulting in a dry coating weight of 0.146 g/m^2. This resulted in the following dry coating composition : 0.197 g/m^2 of Special Schwarz 250 (carbon black available from Degussa), 0.005 g/m2 of Solsperse 5000 (dispersing agent available fron ICI), 0.019 g/m^2 of Solsperse 28000 (dispersing agent available from ICI), 0.019 g/m^2 of Nitrocellulose E950 (available from Wolff Walsrode), 0.007 g/m^2 of Tego Glide 410 (dispersing agent available from Tego Chemie Service GmbH) and 0.003 g/m^2 of Tego Wet 265 (dispersing agent available from Tego Chemie Service GmbH).

[0075] The materials of examples 1,2,3 and 4 were imaged with a CREO Trendsetter 3244T (2400dpi). After imaging the materials were developed at 1 m/min at 25oC in a Technigraph NPX-32T processor using an Ozasol EP262A developer (Ozasol EP262A developer commercially available from Agfa). The IR-exposed areas dissolved very rapidly without any attack in the non IR-exposed areas, resulting in a positive working printing plate. The resulting plates were 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.

[0076] The IR-sensitivity was determined on the processed plates for the four materials i.e. IR-energy density at which the 2x2 pixel check boards closely match a 50 % dot area (densitiy measured with a Macbeth RD918-SB ; density value > 50 % = under exposed ; density value < 50 % = over exposed). The values are listed in table 1. It is clear that the IR-sensitivity is enhanced when using a IR-absorbing compound in the first layer. Increasing the carbon concentration in the top layer (with a comparable amount as used in the first layer of example 3) does not lead to an increase in IR-sensitivity, on the contrary, an IR-sensitivity decrease is observed. This means that the observed increase in IR-sensitivity of examples 2 and 3 cannot be explained just by increasing the optical density (at the exposure wavelength) of the material, but that the presence of the IR-absorbing compound in the first layer is essential in this invention.

Table 1 :

IR-sensitivity and corresponding dot area for the 4 examples			
Example 1 (comparative)	Example 2	Example 3	Example 4 (comparative)
234 mJ/cm2 48 %	186 mJ/cm2 48 %	166 mJ/cm2 48 %	265 mJ/cm2 54 %

Claims

1. A heat mode imaging element for making a lithographic printing plate having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is unpenetrable for or insoluble in an alkaline developer containing SiO_2 in the form of silicates before imagewise IR exposure, imaged parts being capable of removal during development without solubilising and/or damaging non-imaged parts; **characterized in that** said first layer and said top layer comprise a compound capable of converting IR-light into heat.

2. A heat mode imaging element for making a lithographic printing plate according to claim 1 wherein said polymer included in the first layer is a hydrophobic polymer.

3. A heat mode imaging element for making a lithographic printing plate according to claim 2 wherein said hydrophobic polymer is a novolac resin or a polymer comprising hydroxystyrene units.

4. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 3 wherein said first layer further comprises a compound selected from the group consisting of low molecular weight acids and benzophenones.

5. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 4 wherein said compound capable of converting IR-light into heat is an IR dye or pigment.

6. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 5 wherein said compound capable of converting IR-light into heat does not decrease the solubility of the first layer in aqueous alkaline solution.

7. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 6 wherein said compound capable of converting IR-light into heat is present in said first layer in an amount of 0.1 to 30 parts by weight of the total weight of said first layer.

8. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 7 wherein said top layer comprises a binder which is insoluble in an aqueous alkaline solution.

9. A heat mode imaging element for making a lithographic printing plate according to any of claims 5 to 8 wherein said IR dye or pigment is present in said top layer in an amount between 1 and 99 parts by weight of the total weight of said top layer.

10. A method for making a lithographic printing plate comprising the steps of

    a) exposing imagewise to IR-radiation a heat mode imaging element according to any of claims 1 to 9; and
    b) developing said imagewise exposed heat mode imaging element with said alkaline developer whereby the

exposed areas of the first and the top layer are removed and the unexposed areas of the first layer remain.

Patentansprüche

1. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte, das auf einem lithografischen Träger mit einer hydrophilen Oberfläche eine erste Schicht mit einem in einer wäßrig-alkalischen Lösung löslichen Polymer und auf der gleichen Seite des lithografischen Trägers wie die erste Schicht eine Deckschicht enthält, die vor der bildmäßigen IR-Belichtung weder durch einen alkalischen, SiO_2 als Silikate enthaltenden Entwickler durchdringbar ist noch darin löslich ist, wobei die bebilderten Teile während der Entwicklung ohne Solubilisierung und/oder Beschädigung der nicht-bebilderten Teile entfernbar sind, **dadurch gekennzeichnet, daß** die erste Schicht und die Deckschicht eine Verbindung enthalten, die IR-Licht in Wärme umzuwandeln vermag.

2. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach Anspruch 1, **dadurch gekennzeichnet, daß** das in der ersten Schicht enthaltene Polymer ein hydrophobes Polymer ist.

3. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach Anspruch 2, **dadurch gekennzeichnet, daß** das hydrophobe Polymer ein Novolakharz oder ein Hydroxystyroleinheiten enthaltendes Polymer ist.

4. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die erste Schicht weiterhin eine Verbindung aus der Gruppe bestehend aus niedermolekularen Säuren und Benzophenonen enthält.

5. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** die Verbindung, die IR-Licht in Wärme umzuwandeln vermag, ein IR-absorbierender Farbstoff oder ein IR-absorbierendes Pigment ist.

6. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, daß** die Verbindung, die IR-Licht in Wärme umzuwandeln vermag, keine Senkung der Löslichkeit der ersten Schicht in einer wäßrig-alkalischen Lösung bewirkt.

7. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, daß** die Verbindung, die IR-Licht in Wärme umzuwandeln vermag, in einer Menge zwischen 0,1 und 30 Gewichtsteilen, bezogen auf die Gesamtmenge der ersten Schicht, in der ersten Schicht enthalten ist.

8. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, daß** die Deckschicht ein in einer wäßrig-alkalischen Lösung unlösliches Bindemittel enthält.

9. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte nach einem der Ansprüche 5 bis 8, **dadurch gekennzeichnet, daß** der IR-absorbierende Farbstoff oder das IR-absorbierende Pigment in einer Menge zwischen 1 und 99 Gewichtsteilen, bezogen auf die Gesamtmenge der Deckschicht, in der Deckschicht enthalten ist.

10. Ein durch die nachstehenden Schritte gekennzeichnetes Verfahren zur Herstellung einer lithografischen Druckplatte :

    a) bildmäßige Belichtung mit Infrarotstrahlung eines wärmeempfindlichen Bilderzeugungselements nach einem der Ansprüche 1 bis 9, und

    b) Entwicklung des bildmäßig belichteten wärmeempfindlichen Bilderzeugungselements mit dem alkalischen Entwickler, wobei die belichteten Bereiche der ersten Schicht und der Deckschicht entfernt werden und die nicht-belichteten Bereiche der ersten Schicht zurückbleiben.

Revendications

1. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique possédant, sur une base lithographique comprenant une surface hydrophile, une première couche englobant un polymère soluble dans une solution alcaline aqueuse et une couche de protection du même côté de la base lithographique que celui où est située la première couche, ladite couche de protection étant impénétrable pour et insoluble à un révélateur alcalin contenant du SiO_2 sous la forme de silicates avant l'exposition en forme d'image à un rayonnement infrarouge, les parties contenant une image pouvant être éliminées au cours du développement sans donner lieu à une solubilisation et/ou à une dégradation des parties exemptes d'image ; **caractérisé en ce que** ladite première couche et ladite couche de protection comprennent un composé capable de transformer de la lumière infrarouge en chaleur.

2. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon la revendication 1, dans lequel ledit polymère inclus dans la première couche est un polymère hydrophobe.

3. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon la revendication 2, dans lequel ledit polymère est une résine de novolaque ou un polymère comprenant des unités d'hydroxystyrène.

4. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 1 à 3, dans lequel ladite première couche comprend en outre un composé choisi parmi le groupe constitué par des acides à bas poids moléculaire et par des benzophénones.

5. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 1 à 4, dans lequel ledit composé capable de transformer de la lumière infrarouge en chaleur est un colorant ou un pigment infrarouge.

6. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 1 à 5, dans lequel ledit composé capable de transformer de la lumière infrarouge en chaleur ne diminue pas la solubilité de la première couche dans une solution alcaline aqueuse.

7. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 1 à 6, dans lequel ledit composé capable de transformer de la lumière infrarouge en chaleur est présent dans ladite première couche en une quantité de 0,1 à 30 parties en poids du poids total de ladite première couche.

8. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 1 à 7, dans lequel ladite couche de protection comprend un liant qui est insoluble dans une solution alcaline aqueuse.

9. Elément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique selon l'une quelconque des revendications 5 à 8, dans lequel ledit colorant ou ledit liant infrarouge est présent dans ladite couche de protection en une quantité entre 1 et 99 parties en poids du poids total de ladite couche de protection.

10. Procédé de fabrication d'un cliché d'impression lithographique, comprenant les étapes consistant à :

    a) exposer en forme d'image à un rayonnement infrarouge, un élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 9 ; et
    b) développer ledit élément de formation d'image thermosensible exposé en forme d'image avec ledit révélateur alcalin, de telle sorte que les zones exposées de la première couche et de la couche de protection sont éliminées et que les zones non exposées de la première couche subsistent.