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### (54) Processless printing plate with thin oleophilic layer

Verarbeitungsfreie Flachdruckplatte mit einer dünnen oleophilen Schicht

Plaque d'impression lithographique sans traitement contenant une couche oléophile mince

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**Description****FIELD OF THE INVENTION**

5 [0001] The present invention relates to a heat mode recording material for making a lithographic plate for use in lithographic printing. The present invention further relates to a method for imaging said heat mode recording material e.g. by means of a laser.

**BACKGROUND OF THE INVENTION**

10 [0002] Lithographic printing is the process of printing from specially prepared surfaces, some areas of which are capable of accepting ink (oleophilic areas) whereas other areas will not accept ink (hydrophilic areas). According to the so called conventional or wet printing plates, both water or an aqueous dampening liquid and ink are applied to the plate surface that contains hydrophilic and oleophilic areas. The hydrophilic areas will be soaked with water or the dampening liquid and are thereby rendered oleophobic while the oleophilic areas will accept the ink.

15 [0003] When a laser heat mode recording material is to be used as a direct offset master for printing with greasy inks, it is necessary to have oleophilic-hydrophilic mapping of the image and non-image areas. In the case of heat mode laser ablation it is also necessary to completely image wise remove a hydrophilic or oleophilic topcoat to expose the underlying oleophilic respectively hydrophilic surface of the laser sensitive recording material in order to obtain the necessary difference in ink-acceptance between the image and non-image areas.

20 [0004] For example **DE-A- 2 448 325** discloses a laser heat mode "direct negative" printing plate comprising e.g. a polyester film support provided with a hydrophilic surface layer. The disclosed heat mode recording material is imaged using an Argon laser thereby rendering the exposed areas oleophilic. An offset printing plate is thus obtained which can be used on an printing press without further processing. The plate is called a "direct negative" plate because the areas of the recording material that have been exposed are rendered ink accepting.

25 [0005] Other disclosures in **DE-A- 2 448 325** concern "direct negative" printing plates comprising e.g. hydrophilic aluminium support coated with a water soluble laser light (Argon-488nm) absorbing dye or with a coating based on a mixture of hydrophilic polymer and laser light absorbing dye (Argon - 488nm). Further examples about heat mode recording materials for preparing "direct negative" printing plates include e.g. **US-A- 4 341 183**, **DE-A- 2 607 207**, **DD-A- 213 530**, **DD-A- 217 645** and **DD-A- 217 914**. These documents disclose heat mode recording materials that have on an anodized aluminium support a hydrophilic layer. The disclosed heat mode recording materials are image-wise exposed using a laser. Laser exposure renders the exposed areas insoluble and ink receptive, whereas the non exposed image portions remain hydrophilic and water soluble allowing to be removed by the dampening liquid during printing exposing the hydrophilic support. Such plates can be used directly on the press without processing.

30 [0006] **DD-A- 155 407** discloses a laser heat mode "direct negative" printing plate where a hydrophilic aluminum oxide layer is rendered oleophilic by direct laser heat mode imaging. These printing plates may also be used on the press without further processing.

35 [0007] From the above it can be seen that a number of proposals have been made for making a 'direct negative' offset printing plate by laser heat mode recording. They have such disadvantages as low recording speed and/or the obtained plates are of poor quality.

40 [0008] Another way of making direct lithographic plates is by laser ablation

45 [0009] **EP-A- 580 393** discloses a lithographic printing plate directly imageable by laser discharge, the plate comprising a topmost first layer and a second layer underlying the first layer wherein the first layer is characterized by efficient absorption of infrared radiation and the first and second layer exhibit different affinities for at least one printing liquid.

50 [0010] **EP-A- 683 728** discloses a heat mode recording material comprising on a support having an ink receptive surface or being coated with an ink receptive layer a substance capable of converting light into heat and a hardened hydrophilic surface layer having a thickness not more than 3 µm. The lithographic properties of said material are not very good. **WO99/19143** discloses a heat mode printing plate element which comprises a support, an IR-sensitive oleophilic layer and a hydrophilic top layer comprising a cross-linked polymeric matrix containing a colloid of an oxide or hydroxide of a metal and a photothermal conversion material.

**OBJECTS OF THE INVENTION**

55 [0011] It is an object of the present invention to provide a material for a heat mode recording material of high sensitivity and high lithographic quality, especially in regard to a high run length.

## SUMMARY OF THE INVENTION

[0012] According to the present invention there is provided a heat-sensitive material for making lithographic plates comprising in the order given on a hydrophilic surface of a lithographic base an IR-sensitive oleophilic layer and a cross-linked hydrophilic layer comprising a hydrophilic organic polymer, an inorganic pigment and a hardener, wherein said IR-sensitive oleophilic layer amounts to a dry weight between 0.1 and 0.75 g/m<sup>2</sup>.

## DETAILED DESCRIPTION OF THE INVENTION

[0013] In this invention it has been found that by using a lithographic base with a hydrophilic support in combination with a thin oleophilic IR-sensitive layer the run length of the plate can be increased substantially. For these systems the run length is limited by the lithographic properties of the hydrophilic top coating. If the IR-sensitive oleophilic layer is to thin (< 0.1 g/m<sup>2</sup>) the oleophilicity of the exposed areas is low (due to the underlying lithographic base) and the run length will be limited by the imaged areas. If the IR-sensitive oleophilic layer is to thick (>0.75 g/m<sup>2</sup>) the effect of the hydrophilic surface of the lithographic base is lost and the run length will be limited by the non-imaged areas due to toning.

[0014] The IR-sensitive oleophilic layer amounts preferably to a dry weight between 0.15 and 0.5 g/m<sup>2</sup>.

[0015] The IR-sensitive oleophilic layer comprises a binder and a compound capable of converting light into heat.

[0016] Suitable compounds capable of converting light into heat are preferably infrared absorbing components having an absorption in the wavelength range of the light source used for image-wise exposure. Particularly useful compounds are for example dyes and in particular infrared dyes as disclosed in EP-A- 908 307 and pigments and in particular infrared pigments such as 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. WO<sub>2.9</sub>. 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 i.a.on the heat-sensitivity of the imaging element. In this respect it has been found that carbon black or graphite yields very good and favorable results.

[0017] Preferably the polymer is selected from the group consisting of polyvinyl chloride, polyesters, polyurethanes, novolac, polyvinyl carbazole etc., copolymers or mixtures thereof.

[0018] Most preferably the polymeric binder in the recording layer is heat sensitive: e.g. a polymer containing nitrate ester groups (e.g. self oxidizing binder cellulose nitrate as disclosed in GB-P- 1 316 398 and DE-A- 2 512 038); e.g. a polymer containing carbonate groups (e.g. polyalkylene carbonate); e.g. a polymer containing covalently bound chlorine (e.g. polyvinylidene chloride). Also substances containing azo or azide groups , capable of liberating N<sub>2</sub> upon heating are favourably used.

[0019] Different kinds of hardened hydrophilic surface layers are suitable in connection with the present invention: The hydrophilic coatings are preferably cast from aqueous compositions containing hydrophilic binders having free reactive groups including e.g. hydroxyl, carboxyl, hydroxyethyl, hydroxypropyl, amino, aminoethyl, aminopropyl, carboxymethyl, etc.. along with suitable crosslinking or modifying agents including e.g. hydrophilic organotitanium reagents, aluminoformyl acetate, dimethylol urea, melamines, aldehydes, hydrolyzed tetraalkyl orthosilicate, etc..

[0020] Suitable polymers for hydrophilic layers may be selected from the group consisting of gum arabic, casein, gelatin, starch derivatives, carboxymethyl cellulose and Na salt thereof, cellulose acetate, sodium alginate, vinyl acetate-maleic acid copolymers, styrene-maleic acid copolymers, polyacrylic acids and salts thereof, polymethacrylic acids and salts thereof, hydroxyethylene polymers, polyethylene glycols, hydroxypropylene polymers, polyvinyl alcohols, and hydrolyzed polyvinylacetate having a hydrolyzation degree of at least 60% by weight and more preferably at least 80% by weight.

[0021] Hydrophilic layers containing polyvinylalcohol or polyvinylacetate hydrolyzed to an extent of at least 60% by weight hardened with a tetraalkyl orthosilicate, e.g. tetraethyl orthosilicate or tetramethyl orthosilicate, as disclosed in e.g. US-P- 3 476 937 are particularly preferred because their use in the present heat mode recording material results in excellent lithographic printing properties.

[0022] A further suitable hardened hydrophilic surface layer is disclosed in EP-A- 514 990. The hydrophilic layer disclosed in this EP-application comprises the hardening reaction product of a (co)polymer containing amine or amide functions having at least one free hydrogen (e.g. amino modified dextrane) and aldehyde.

[0023] A cross-linked hydrophilic binder in the heat-sensitive layer used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer e.g. metal oxide colloid particles which are particles of titanium dioxide or other metal oxides. Incorporation of these particles gives the surface of the cross-linked hydrophilic layer a uniform rough texture consisting of microscopic hills and valleys. Preferably these particles are oxides or hydroxides of beryllium, magnesium, aluminium, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth or a transition metal. Particularly preferable colloid particles are oxides or hydroxides of aluminum, silicon, zirconium and titanium, used in 20 to 95 % by weight of the hydrophilic

layer, more preferably in 30 to 90% by weight of the hydrophilic layer.

[0024] The cross-linked hydrophilic layer is preferably coated at a dry thickness of 0.3 to 5 µm, more preferably at a dry thickness of 0.5 to 3 µm.

[0025] According to the present invention the hardened hydrophilic layer may comprise additional substances such as e.g. plasticizers, pigments, dyes etc.. The cross-linked hydrophilic layer can additionally contain an IR-absorbing compound in order to increase the IR-sensitivity. 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**.

[0026] According to the present invention, the lithographic base may be an anodised aluminum support. 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**.

[0027] According to another mode in connection with the present invention, the lithographic base with a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film or aluminum, 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 tetra-alkylorthosilicate. The latter is particularly preferred.

[0028] 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, acrylate acid, methacrylate 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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**.

[0033] 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, substrated polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent. Also suitable as flexible support is glass with a thickness less than 1.2 mm and a failure stress (under tensile stress) equal or higher than  $5 \times 10^7$ .

[0034] 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<sup>2</sup> and 750 mg per m<sup>2</sup>. 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<sup>2</sup> per gram, more preferably at least 500 m<sup>2</sup> per gram.

**[0035]** In accordance with the present invention the imaging element is image-wise exposed. During said exposure, in the exposed areas the cross-linked hydrophilic layer can be removed and said areas are converted to oleophilic areas while the unexposed areas remain hydrophilic. This is mostly the case when using short pixel dwell times (for example 1 to 100 ns). However when using longer pixel dwell times (for example 1 to 20 µs) the hydrophilic layer is not or only partially removed upon exposure. The remaining parts of the hydrophilic layer can be removed on the press by contact with fountain solution and ink or by an additional wet or dry processing step between the IR-laser exposure and the start-up of the printing process.

**[0036]** Image-wise exposure in connection with the present invention is preferably an image-wise scanning exposure involving the use of a laser or L.E.D. Preferably used are lasers that operate in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared with an intensity greater than 0.1 mW/µm<sup>2</sup>.

**[0037]** According to the present invention the plate is then ready for printing without an additional development and can be mounted on the printing press.

**[0038]** According to a further method, the imaging element is first mounted on the printing cylinder of the printing press and then image-wise exposed directly on the press. Subsequent to exposure, the imaging element is ready for printing.

**[0039]** 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 mounting a conventional printing plate. More details on sleeves are given in "Grafisch Nieuws", 15, 1995, page 4 to 6.

**[0040]** The following example illustrates the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

#### EXAMPLE

##### Preparation of the lithographic base

**[0041]** A 0.30 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/m<sup>2</sup> to form a surface topography with an average center-line roughness Ra of 0.5 mm.

**[0042]** 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.

**[0043]** 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<sup>2</sup> for about 300 seconds to form an anodic oxidation film of 3.00 g/m<sup>2</sup> of Al<sub>2</sub>O<sub>3</sub> then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and subsequently with a solution containing aluminum trichloride, rinsed with demineralized water at 20°C during 120 seconds and dried.

**[0044]** On top of said lithographic base was coated the IR-sensitive layer to a wet coating thickness of 35 µm from a solution having the following composition:

279.3g	Carbon black dispersion of the following composition
34.9 g	Special Schwarz™ (Degussa)
3.5 g	Nitrocellulose E950™ (Wolf Walsrode)
4.2 g	Dispersing agent
236.7 g	Methyl ethyl ketone
217.8g	Nitrocellulose solution of the following composition
21.8 g	Nitrocellulose E950™
196.0 g	Ethylacetate
24.0g	Cymel solution of the following composition
4.8 g	Cymel 301™
19.2 g	Ethylacetate
8.75g	p-toluene sulphonic acid solution of the following composition
0.875 g	p-toluene sulphonic acid
7.875 g	Ethylacetate

[0045] After drying the IR-sensitive layer, the hydrophilic layer was coated to a wet coating thickness of 20  $\mu\text{m}$  from a solution having the following composition

5      67.7 g    TiO<sub>2</sub>- dispersion in water, stabilized with Polyviol WX 48™ (polyvinyl alcohol from Wacker) (10 % w/w polyvinyl alcohol versus TiO<sub>2</sub>) ( average particle size 0.3 to 0.5  $\mu\text{m}$ )-6.25% w/w  
 10     32.3 g    hydrolyzed tetramethyl orthosilicate in water/ethanol-6.25% w/w  
 1.2g    wetting agent in water-5%w/w

[0046] The pH of this solution was adjusted to 4 prior to coating. This layer was hardened for 12 hours at 67°C/ 50% R.H.. In this way the reference element was obtained.

[0047] The elements 1, 2, 3, 4, 5, 6 and 7 were prepared in an identical way as the reference element with as only difference the thickness of the oleophilic layer. The thickness is given in table 1.

[0048] The resulting imaging elements were imaged on a Gerber C42 T™ at 2400 dpi operating at a scanning speed of 150 rps and a laser output of 7.5 Watt

[0049] After imaging the plate was mounted on a Sakurai Oliver 52 press using K+E 800 Skinnex as ink and 4% Aqua ayde + 3% Tame as fountain solution. A non-compressible blanket was used.

[0050] Subsequently the press was started by allowing the print cylinder with the imaging element mounted thereon to rotate. The dampener rollers of the press were first dropped on the imaging element so as to supply dampening liquid to the imaging element and after 10 revolutions of the print cylinder, the ink rollers were dropped to supply ink.

20     After 10 further revolutions paper was feeded. The run length was determined based on the number of sheets that could be printed without toning. The results are summarised in table 1. It is clear that the imaging elements with an oleophilic layer of 0.3 and 0.55 g/m<sup>2</sup> give a much higher run length. If the oleophilic layer is to thin (0.05 g/m<sup>2</sup>) the run length is limited by the imaged areas. Thicker oleophilic layers (0.8 g/m<sup>2</sup> and more) lead to a reduced run length of the non-imaged areas.

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Table 1

Element	Coating thickness oleophilic layer	Run length
1	0.05 g/m <sup>2</sup>	2,000
2	0.3 g/m <sup>2</sup>	20,000
3	0.55 g/m <sup>2</sup>	12,000
4	0.8 g/m <sup>2</sup>	7,000
5	1.86g/m <sup>2</sup>	5,000
6	2.5 g/m <sup>2</sup>	3,000
7	3.5 g/m <sup>2</sup>	5,000
8	0.3 g/m <sup>2</sup>	5,000

[0051] Element 8 was prepared in an identical way as element 2 with the exception that the grained and anodized aluminum substrate was replaced by an untreated aluminum support. The run length is low compared with element 2. This clearly demonstrates the necessity of the combination of a lithographic base with a thin IR-sensitive oleophilic layer.

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## Claims

1. A heat-sensitive material for making lithographic plates comprising in the order given on a hydrophilic surface of a lithographic base an IR-sensitive oleophilic layer and a cross-linked hydrophilic layer comprising a hydrophilic organic polymer, an inorganic pigment and a hardener, wherein said IR-sensitive oleophilic layer amounts to a dry weight between 0.1 and 0.75 g/m<sup>2</sup>.
2. A heat-sensitive material according to claim 1 wherein said IR-sensitive oleophilic layer amounts to a dry weight between 0.15 and 0.5 g/m<sup>2</sup>.
3. A heat-sensitive material according to claim 1 or 2 wherein said oleophilic layer comprises a binder and a compound capable of converting light into heat.

4. A heat-sensitive material according to claim 3 wherein said oleophilic binder is heat sensitive.

5. A heat-sensitive material according to claim 3 or 4 wherein said compound capable of converting light into heat is carbon black or graphite.

6. A heat-sensitive material according to any of claims 1 to 5 wherein said cross-linked hydrophilic layer comprises oxides or hydroxydes of beryllium, magnesium, aluminium, silicon, gadolinium, germanium, arsenic, indium, tin, antimony, tellurium, lead, bismuth, titanium or a transition metal.

10. 7. A heat-sensitive material according to any of claims 1 to 6 wherein said lithographic base is a grained and anodized aluminum support.

8. A heat-sensitive material according to any of claims 1 to 6 wherein said lithographic base is a cross-linked hydrophilic layer on a flexible support.

15. 9. A heat-sensitive material according to any of claims 1 to 8 wherein the hydrophilic layer has a dry thickness between 0.3 and 5 µm.

20. 10. A method for making lithographic printing plates comprising the steps of (i) image-wise exposing to a laser beam having an intensity greater than 0.1 mW/µm<sup>2</sup> a heat sensitive material according to any of claims 1 to 9; (ii) before or after step (i) mounting the plate on a printing press; (iii) contacting the plate with fountain solution and ink.

#### Patentansprüche

1. Ein wärmeempfindliches Material zur Herstellung von lithografischen Druckplatten, wobei das Material der Reihe nach auf einer hydrophilen Oberfläche einer lithografischen Unterlage eine IR-empfindliche oleophile Schicht und eine vernetzte hydrophile Schicht mit einem hydrophilen organischen Polymer, einem anorganischen Pigment und einem Härtner enthält, **dadurch gekennzeichnet, dass** die IR-empfindliche oleophile Schicht in einem Trockengewicht zwischen 0,1 und 0,75 g/m<sup>2</sup> verwendet wird.

2. Wärmeempfindliches Material nach Anspruch 1, **dadurch gekennzeichnet, dass** die gegenüber Infrarotstrahlung empfindliche oleophile Schicht in einem Trockengewicht zwischen 0,15 und 0,5 g/m<sup>2</sup> aufgetragen wird.

3. Wärmeempfindliches Material nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die oleophile Schicht ein Bindemittel und eine Verbindung, die Licht in Wärme umzuwandeln vermag, enthält.

4. Wärmeempfindliches Material nach Anspruch 3, **dadurch gekennzeichnet, dass** das oleophile Bindemittel wärmeempfindlich ist.

5. Wärmeempfindliches Material nach Anspruch 3 oder 4, **dadurch gekennzeichnet, dass** die Verbindung, die Licht in Wärme umzuwandeln vermag, Ruß oder Grafit ist.

6. Wärmeempfindliches Material nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die vernetzte hydrophile Schicht Oxide oder Hydroxide von Beryllium, Magnesium, Aluminium, Silicium, Gadolinium, Germanium, Arsen, Indium, Zinn, Antimon, Tellur, Blei, Wismut, Titan oder einem Übergangsmetall enthält.

7. Wärmeempfindliches Material nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die lithografische Unterlage ein gekörnter und eloxierter Aluminiumträger ist.

8. Wärmeempfindliches Material nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die lithografische Unterlage eine vernetzte hydrophile Schicht auf einem biegsamen Träger ist.

9. Wärmeempfindliches Material nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** die hydrophile Schicht eine Trockenschichtstärke zwischen 0,3 und 5 µm aufweist.

10. Ein durch die nachstehenden Schritte **gekennzeichnetes** Verfahren zur Herstellung von lithografischen Druckplatten : (i) bildmäßige Belichtung eines wärmeempfindlichen Materials nach einem der Ansprüche 1 bis 9

mit einem Laserstrahl mit einer Stärke von mehr als  $0,1 \text{ mW}/\mu\text{m}^2$ , (ii) vor oder nach Schritt (i) das Einspannen der Platte in eine Druckpresse und (iii) das Inkontaktbringen der Platte mit Feuchtwasser und Druckfarbe.

5 **Revendications**

1. Matériau thermosensible pour la fabrication de clichés lithographiques, comprenant, dans l'ordre donné, sur la surface hydrophile d'une base lithographique, une couche oléophile sensible au rayonnement infrarouge et une couche hydrophile réticulée comprenant un polymère organique hydrophile, un pigment inorganique et un durcisseur, la quantité de ladite couche oléophile sensible au rayonnement infrarouge étant telle que l'on obtient un poids à sec entre 0,1 et  $0,75 \text{ g}/\text{m}^2$ .
2. Matériau thermosensible selon la revendication 1, dans lequel ladite couche oléophile sensible au rayonnement infrarouge est utilisée en une quantité telle que l'on obtient un poids à sec entre 0,15 et  $0,5 \text{ g}/\text{m}^2$ .
3. Matériau thermosensible selon la revendication 1 ou 2, dans lequel ladite couche oléophile comprend un liant et un composé capable de transformer de la lumière en chaleur.
4. Matériau thermosensible selon la revendication 3, dans lequel ledit liant oléophile est thermosensible.
5. Matériau thermosensible selon la revendication 3 ou 4, dans lequel ledit composé capable de transformer de la lumière en chaleur est du noir de carbone ou du graphite.
6. Matériau thermosensible selon l'une quelconque des revendications 1 à 5, dans lequel ladite couche hydrophile réticulée comprend des oxydes ou des hydroxydes du beryllium, du magnésium, de l'aluminium, du silicium, du gadolinium, du germanium, de l'arsenic, de l'indium, de l'étain, de l'antimoine, du tellure, du plomb, du bismuth, du titane ou d'un métal de transition.
7. Matériau thermosensible selon l'une quelconque des revendications 1 à 6, dans lequel ladite base lithographique est un support en aluminium grainé et anodisé.
8. Matériau thermosensible selon l'une quelconque des revendications 1 à 7, dans lequel ladite base lithographique est une couche hydrophile réticulée sur un support flexible.
9. Matériau thermosensible selon l'une quelconque des revendications 1 à 8, dans lequel la couche hydrophile possède une épaisseur à sec entre 0,3 et  $5 \mu\text{m}$ .
10. Procédé pour fabriquer des clichés d'impression lithographique, comprenant les étapes consistant à (i) exposer en forme d'image à un faisceau laser possédant une intensité supérieure à  $0,1 \text{ mW}/\mu\text{m}^2$ , un matériau thermosensible selon l'une quelconque des revendications 1 à 9 ; (ii) avant ou après l'étape (i), monter le cliché sur une presse d'impression ; (iii) mettre ledit cliché en contact avec une solution de mouillage et avec de l'encre.

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