Method for making a processless lithographic printing plate
Verfahren zur Herstellung einer verarbeitungsfreien Flachdruckplatte
Procédé de fabrication d’une plaque d’impression lithographique sans traitement

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FIELD OF THE INVENTION

The present invention relates to a method for making a negative-working, heat-sensitive printing plate precursor which is suitable for making a lithographic printing plate by direct-to-plate recording.

BACKGROUND OF THE INVENTION

Lithographic printing presses use a so-called printing master such as a printing plate which is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a print is obtained by applying ink to said image and then transferring the ink from the master onto a receiver material, which is typically paper. In conventional, so-called "wet" lithographic printing, ink as well as an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-accepting, ink-repelling) areas. In so-called driographic printing, the lithographic image consists of ink-accepting and ink-adhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

Printing masters are generally obtained by the image-wise exposure and processing of an imaging material called plate precursor. In addition to the well-known photosensitive, so-called pre-sensitized plates, which are suitable for UV contact exposure through a film mask, also heat-sensitive printing plate precursors have become very popular in the late 1990s. Such thermal materials offer the advantage of daylight stability and are especially used in the so-called computer-to-plate method wherein the plate precursor is directly exposed, i.e. without the use of a film mask. The material is exposed to heat or to infrared light and the generated heat triggers a (physico-) chemical process, such as ablation, polymerization, insolubilization by cross linking of a polymer, heat-induced solubilization, or by particle coagulation of a thermoplastic polymer latex.

The most popular thermal plates form an image by a heat-induced solubility difference in an alkaline developer between exposed and non-exposed areas of the coating. The coating typically comprises an oleophilic binder, e.g. a phenolic resin, of which the rate of dissolution in the developer is either reduced (negative working) or increased (positive working) by the image-wise exposure. During processing, the solubility differential leads to the removal of the non-image (non-printing) areas of the coating, thereby revealing the hydrophilic support, while the image (printing) areas of the coating remain on the support. Typical examples of such plates are described in e.g. EP-A 625728, 823327, 825927, 864420, 894622 and 901902. Negative working embodiments of such thermal materials often require a pre-heating step between exposure and development as described in e.g. EP-A 625,728.

Some of these thermal processes enable plate making without wet processing and are for example based on ablation of one or more layers of the coating. At the exposed areas the surface of an underlying layer is revealed which has a different affinity towards ink or fountain than the surface of the unexposed coating; the image (printing) and non-image or background (non-printing) areas are obtained.

US 5,605,780 discloses a lithographic printing plate comprising an anodized aluminum support and provided thereon an image-forming layer comprising an IR absorbing agent and a cyanoacrylate polymer binder. The image-forming layer is removed by laser-induced thermal ablation whereby the underlying hydrophilic support is revealed.

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.

EP 1,065,051 discloses a negative-working heat-sensitive material for making lithographic plates comprising in the order given a lithographic base having a hydrophilic surface, an oleophilic imaging layer and a cross-linked hydrophilic upper layer. The heat generated during exposure in the light-sensitive layer removes the hydrophilic upper layer by ablation.

Most ablative plates generate ablation debris which may contaminate the electronics and optics of the exposure device and which needs to be removed from the plate by wiping it with a cleaning solvent, so that ablative plates are often not truly processless. Ablation debris which is deposited onto the plate’s surface may also interfere during the printing process and result in for example scumming.

Other thermal processes which enable plate making without wet processing are for example processes based on a heat-induced hydrophilic/ oleophilic conversion of one or more layers of the coating so that at exposed areas a different affinity towards ink or fountain is created than at the surface of the unexposed coating.

US 5,855,173, US 5,839,369 and 5,839,370 describe a method relying on the image-wise hydrophilic-hydrophobic transition of a ceramic such as a zirconia ceramic and the subsequent reverse transition in an image erasure step. This image-wise transition is obtained by exposure to infrared laser irradiation at a wavelength of 1064 nm at high power which induces local ablation and formation of substoichiometric zirconia. US 5,893,328, US 5,836,248 and US
According to the present invention there is further provided a method for making a lithographic printing plate comprising the steps of

(i) providing a lithographic printing plate precursor according to the present invention;

(ii) image-wise exposing the precursor to heat and/or infrared light whereby the surface of the precursor switches from a hydrophilic state to a hydrophobic state at exposed areas.

[0022] According to the present invention there is further provided a method of printing comprising the steps of
According to the method of the present invention, a printing plate precursor having a support with a surface comprising titanium is converted from a hydrophobic state into a hydrophilic state by first anodizing and then annealing said surface under reduced pressure. By irradiation of the hydrophilized surface with heat and/or infrared light, a switch from a hydrophilic state into a hydrophobic state is obtained.

The support of the printing plate precursor having a surface comprising titanium is preferably a titanium metal sheet. Alternatively, the support is a base onto which a thin layer of titanium metal is applied.

The titanium metal sheet may be a commercially available titanium metal sheet having preferably a 99.5 %wt to 99.9 %wt purity. Also suitable is an alloy of titanium containing about 4 %wt to 5 %wt of for example aluminium, vanadium, manganese, iron, chromium and molybdenum. The thickness of the titanium metal sheet is not critical: it may be between 0.05 mm to 0.6 mm, preferably from 0.05 mm to 0.4 mm, more preferably from 0.1 mm to 0.3 mm.

The base onto which a titanium layer is applied may be a metal sheet including for example aluminium, stainless steel, nickel, and copper. Also suitable as a base is a flexible plastic support such as polyester or cellulose ester, waterproof paper, polyethylene-laminated paper, or polyethylene-impregnated paper. The support can also be a laminate comprising an aluminum foil and a plastic layer, e.g. polyester film.

When a metal sheet is used as a base for the titanium layer, the surface of the metal base may have been roughened by any of the known methods. The surface roughening may be conducted by mechanical means, electro-chemical means and chemical etching means, or by combinations of these methods.

A particularly preferred lithographic support is an electrochemically grained and anodized aluminum support. The grained and anodized aluminum support is preferably grained by electrochemical graining, and anodized by means of anodizing techniques employing phosphoric acid or a sulphuric acid/phosphoric acid mixture. Methods of both graining and anodization of aluminum are very well known in the art.

By varying the type and/or concentration of the electrolyte and the applied voltage in the graining step, different type of grains can be obtained.

By anodizing the aluminium support, its abrasion resistance and hydrophilic nature are improved. The microstructure as well as the thickness of the Al₂O₃ layer are determined by the anodizing step, the anodic weight (g/m² A1203 formed on the aluminium surface) varies between 1 and 8 g/m².

The thin layer of titanium present on the base may be applied by known methods such as for example vapor deposition, spray pyrolysis, sputtering, or electrodeposition. The thickness of the deposited titanium metal layer is preferably from 0.01 μm to 10 μm, more preferably from 0.05 μm to 1.0 μm, most preferably the thickness varies between 0.10 μm and 0.30 μm.

The titanium sheet or the base provided with a titanium layer may be subjected to a surface roughening step treatment prior to the anodization step. Preceding the surface-roughening step, a degreasing step may be conducted with for example a surfactant, an organic solvent or an aqueous alkali solution.

The surface roughening treatment of the titanium sheet or the base provided with a titanium layer can be conducted by various methods; examples thereof include mechanically roughening (e.g. grinding with balls, brushing, blasting, or buffing), electrochemical dissolution (e.g. surface roughening in an electrolytic solution with application of an AC or DC current) or chemical dissolution (e.g. immersing the metal in an aqueous solution of one or more alkaline salts selected from sodium hydroxide, sodium carbonate, sodium silicate or sodium pyrophosphate). These methods may be used alone or in combination.

According to a preferred method of the present invention, the anodization of titanium is performed by treatment of the surface comprising titanium with an aqueous electrolyte solution at a concentration of 0.001 mol/l to 5 mol/l, preferably from 0.005 mol/l to 3 mol/l, a liquid temperature of 5°C to 70°C, preferably from 15°C to 30°C, a DC voltage of 1 V to 100 V, preferably 5 V to 50 V, more preferably 10 V to 30 V, and an electrolysis period of 10 seconds to 10 minutes, preferably 1 minute to 8 minutes.

More preferably, the surface of the support is anodized in an aqueous electrolyte solution containing at least one of the following chemicals:
• an inorganic acid selected from sulfuric acid, phosphoric acid, nitric acid or boric acid;
• hydrogen peroxide in addition to one or more of these inorganic acids;
• an alkali metal salt and/or an alkaline earth metal salt of these inorganic acids;
• an organic acid selected from oxalic acid, tartaric acid, citric acid, acetic acid, lactic acid, succinic acid, glutamic acid, sulfosalicyclic acid or napthalenedisulfonic acid;
• an alkali metal salt and/or an alkaline earth metal salt of these organic acids.
• hydroxides and/or water-soluble carbonates of sodium, potassium, calcium, lithium, and magnesium and/or aqueous alkali solutions such as ammonium hydroxide solution;
• glycerophosphoric acid and the alkali metal salt and/or the alkaline earth metal salt thereof and/or acetic acid and the alkali metal salt and/or the alkaline earth metal salt thereof.

[0037] These aqueous electrolyte solutions may be used alone or in combination. The concentration of the solutions depends on the kind of the electrolyte used for the anodization process.
[0038] In a most preferred embodiment the electrolyte solution comprises oxalic acid at a concentration of 0.6 mol/l, and the anodizing reaction is carried out at room temperature using 20 V DC for a period of 5 minutes.
[0039] Doping the anodized surface with a metal such as platinum, palladium, gold, silver, copper, nickel, iron, or cobalt or a mixture thereof may be advantageous.
[0040] According to the method of the present invention, the anodized support is annealed at a reduced atmospheric pressure. Other gasses such as H₂ or N₂ gas may be used during the annealing step.
[0041] Preferably the annealing temperature varies between 350°C and 550°C, more preferably between 400 °C and 500°C, and the annealing time varies between 60 minutes and 240 minutes, more preferably between 80 and 200 minutes. The pressure applied during the annealing step varies between 0.1 kPa (1 mBar) and 1 kPa (10 mBar), more preferably between 0.2 kPa (2 mBar) and 0.6 kPa (6 mBar).
[0042] The lithographic printing plate precursor comprising an anodized and annealed support thus obtained, may be rinsed with water, with a liquid containing a surfactant or with a desensitizing liquid (so called gum solution) containing gum arabic or a starch derivative, or with combinations thereof.
[0043] The surface of the printing plate precursor is hydrophilic and upon image-wise exposure to heat and/or light, the exposed areas become ink accepting. This conversion from a hydrophilic to a hydrophobic state can for example be characterized by an increase of the contact angle for water measured on the surface: the contact angle for water increases after the treatment of the support indicating a hydrophilic/hydrophobic conversion. The contact angle is defined as the angle between the tangent of the edge of the water droplet at the contact zone between the support and the droplet.
[0044] A layer which comprises a compound capable of absorbing light and converting the absorbed energy into heat may optionally be coated onto the anodized and annealed support or onto the etched and anodized support. The compound capable of absorbing light and converting it into heat is preferably an infrared absorbing agent. Preferred IR absorbing compounds are dyes such as cyanine, mercocyanine, indoaniline, oxonol, pyrilium and squarilium dyes or pigments such as carbon black. Examples of suitable IR absorbers are described in e.g. EP-As 823327, 978376, 1029667, 1053868, 1093934; WO 97/39894 and 00/29214. A preferred compound is the following cyanine dye IR-A:

\[
\text{IR-A:} \quad X^-
\]

wherein X⁻ is a suitable counter ion such as tosylate.
[0045] The coating may in addition to the layer comprising the infrared absorbing agent also contain one or more additional layer(s) such as i.e. a protective layer or an adhesion-improving layer between the layer comprising the infrared absorbing agent and the support.
[0046] Optionally, the layer comprising a compound capable of absorbing light or an optional other layer may further contain additional ingredients. For example binders, surfactants such as perfluoro surfactants, silicon or titanium dioxide particles or colorants may be present.
According to the present invention, the heat-sensitive printing plate precursor thus obtained is then image-wise exposed directly with heat or indirectly with infrared light, preferably near infrared light. The infrared light is preferably converted into heat by an IR light absorbing compound as discussed above. The printing plate precursor is not sensitive to ambient light so that it can be handled without the need for a safe light environment.

The printing plate precursor can be exposed to infrared light by means of e.g. LEDs or an infrared laser. Preferably, the light used for the exposure is a laser emitting near infrared light having a wavelength in the range from about 700 nm to about 1500 nm, e.g. a semiconductor laser diode, a Nd:YAG or a Nd:YLF laser.

The exposure step may optionally be followed by a rinsing step and/or a gumming step. The gumming step involves post-treatment of the heat-sensitive printing plate with a gum solution. A gum solution is typically an aqueous liquid which comprises one or more surface protective compounds that are capable of protecting the lithographic image of a heat-sensitive material or printing plate against contamination or damaging. Suitable examples of such compounds are film-forming hydrophilic polymers or surfactants.

According to the present invention, the heat-sensitive printing plate is then ready for printing without an additional development step. The exposed plate can be mounted on a conventional, so-called wet offset printing press in which ink and an aqueous dampening liquid are supplied to the material. The non-image areas hold the dampening water and the image areas withhold the ink.

Another suitable printing method uses so-called single-fluid ink without a dampening liquid. Suitable single-fluid inks have been described in US 4,045,232; US 4,981,517 and US 6,140,392. In a most preferred embodiment, the single-fluid ink comprises an ink phase, also called the hydrophobic or oleophilic phase, and a polyol phase as described in WO 00/32705.

Alternatively, the printing plate is first mounted on the printing cylinder of the printing press and then image-wise exposed directly on the press by means of an integrated image-recording device. Subsequent to exposure, the plate is ready for printing.

The printing plate can be regenerated after printing. After printing, the printing plate is subjected to a flood exposure with UV light whereby hydrophobic areas are converted to a hydrophilic state and recover sensitivity to infrared light and/or heat irradiation. Optionally, before the flood exposure step, a cleaning step may be performed to remove the adherent ink. Suitable solvents that can be used for cleaning include hydrophobic petroleum solvents such as aromatic hydrocarbons commercially available as printing ink solvents: kerosine, benzol, toluol, xylol, acetone, methyl ethyl ketone, and mixtures thereof.

The regenerated printing plate precursor thus obtained can be used for a next printing operation involving image-wise exposure and printing.

Examples

Example 1.

A titanium foil (Goodfellow T1000380 99.6%, 125 µm foil) was cleaned by ultrasound treatment in isopropanol and was subsequently rinsed with water.

Samples with a size of 19 cm x 5.5 cm were cut out of the cleaned titanium support and anodized using a counter electrode of titanium and a distance between the two electrodes of 2.4 cm. Table 1 lists the different anodizing conditions. Printing plate precursors 1 and 3 were anodized in one single step whereas printing plate precursor 2 was anodized in three subsequent steps. Every anodizing step was followed by a rinsing step with water.

<table>
<thead>
<tr>
<th>Table 1: Anodizing conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodizing conditions</td>
</tr>
<tr>
<td>Printing plate precursor (PPP) nr.</td>
</tr>
<tr>
<td>PPP 1</td>
</tr>
<tr>
<td>PPP 2</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PPP 3</td>
</tr>
</tbody>
</table>

*:RT = room temperature

The precursors subsequently underwent two different annealing treatments in air at a reduced pressure:
1) *(0.21 - 0.5 kPa) at 430°C during 90 minutes and
2) *(0.21 - 0.5 kPa) at 430°C during 180 minutes

[0058] The thus obtained printing plate precursors 1, 2 and 3 were subsequently irradiated with a single beam IR-laser diode at 830 nm with a pitch of 7 μm at 280 mW at 4 m/s (corresponding to an energy density of 1000 mJ/cm²) and with a single beam IR-laser diode at 830 nm with a pitch of 7 μm at 280 mW at 8 m/s (corresponding to an energy density of 500 mJ/cm²).

[0059] After irradiation, the contact angles of the printing plates 1, 2 and 3 were measured with a water droplet utilizing a Fibro DAT1100 equipment (trademark of FIBRO system AB). The contact angles were measured 2 ms after the deposition of the water droplet and are summarized in Table 2. * = 2.10-5 mBar

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**Table 2: Contact angles before and after the annealing step.**

<table>
<thead>
<tr>
<th>Printing plate nr.</th>
<th>Annealing step</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing plate 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>No annealing</td>
<td>50°</td>
</tr>
<tr>
<td>Invention</td>
<td>90 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>33°</td>
</tr>
<tr>
<td>Invention</td>
<td>180 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>38°</td>
</tr>
<tr>
<td>Printing plate 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>No annealing</td>
<td>51°</td>
</tr>
<tr>
<td>Invention</td>
<td>90 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>34°</td>
</tr>
<tr>
<td>Invention</td>
<td>180 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>31°</td>
</tr>
<tr>
<td>Printing plate 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>No annealing</td>
<td>42°</td>
</tr>
<tr>
<td>Invention</td>
<td>90 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>28°</td>
</tr>
<tr>
<td>Invention</td>
<td>180 min, 430°C, *(0.21 - 0.5 kPa)</td>
<td>27°</td>
</tr>
</tbody>
</table>

* = 2.10-5 mBar

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[0060] The results of Table 2 indicate that the annealing step under reduced pressure of the printing plate precursors results in a lowering of the contact angle value.

[0061] Upon laser irradiation of printing plate precursor 3 (non annealed sample and annealed sample), printing plate 3 is obtained of which the contact angle remains the same for the non-annealed plate and increases for the annealed plates indicating a hydrophilic/hydrophobic switch (Table 3).

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**Table 3: Contact angles after laser irradiation.**

<table>
<thead>
<tr>
<th>Printing plate</th>
<th>Annealing step</th>
<th>Contact angle after IR-laser irradiation mJ/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Printing plate 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative</td>
<td>No annealing</td>
<td>42°</td>
</tr>
<tr>
<td>Invention</td>
<td>90 min, 430°C, 2.10-5 mBar</td>
<td>28°</td>
</tr>
<tr>
<td>Invention</td>
<td>180 min, 430°C, 2.10-5 mBar</td>
<td>27°</td>
</tr>
</tbody>
</table>

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**Claims**

1. A method for making a negative-working, heat sensitive lithographic printing plate precursor comprising the steps of

(i) providing a support having a surface comprising titanium,
(ii) modifying said surface by producing a hydrophilic oxide of titanium by the steps of
1) anodizing said surface and
2) annealing said anodized surface under reduced pressure,

wherein said oxide of titanium is capable of switching from a hydrophilic state to a hydrophobic state upon exposure to heat and/or infrared light.

2. A method according to claim 1 wherein the anodizing step is carried out by subjecting the surface at room temperature for a period of 1 to 8 minutes in an aqueous electrolyte solution at a concentration of 0.005 mol/l to 3 mol/l to a DC voltage of 10 V to 30 V.

3. A method according to claim 1 or 2 wherein the annealing step is carried out for a period of 60 to 240 minutes, at a temperature between 350 and 550 °C and a pressure between 1m Bar to 10m Bar (0.1kPa to 1kPa).

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

(i) providing a lithographic printing plate precursor obtained according to the method of any of the preceding claims;
(ii) image-wise exposing the precursor to heat and/or infrared light whereby the surface of the precursor switches from a hydrophilic state to a hydrophobic state at exposed areas, thereby producing a lithographic image on said surface.

5. A lithographic printing method comprising the steps of

(i) providing a lithographic printing plate according to the method of claim 4;
(ii) producing a plurality of printed copies by supplying ink to the printing plate and transferring the ink to paper;
(iii) optionally cleaning the printing plate by removing the ink from the plate;
(iv) erasing the lithographic image by flood-exposing the printing plate to UV light thereby converting hydrophobic areas of the surface to a hydrophilic state;
(v) re-using the precursor thus obtained in a next cycle comprising steps (i) to (iv).

Patentansprüche

1. Ein durch die nachstehenden Schritte gekennzeichnetes Verfahren zur Herstellung einer negativarbeitenden wärmeempfindlichen lithografischen Druckplattenvorstufe:

(i) Bereitstellen eines Trägers mit einer titanhaltigen Oberfläche,
(ii) Modifizieren der Oberfläche durch Herstellung eines hydrophilen Titanoxids, wobei dieser Prozess folgende Schritte umfasst:

1) Anodisieren der Oberfläche und
2) Tempern der anodisierten Oberfläche unter vermindertem Druck,

wobei das Titanoxid bei Erwärmung und/oder Belichtung mit Infrarotlicht von hydrophil in hydrophob umgewandelt werden kann.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass der Anodisierungsschritt aus einer Verarbeitung der Oberfläche bei Zimmertemperatur in einer wässrigen Elektrolytlösung besteht, wobei die Elektrolysedauer 1 Minute bis 8 Minuten, das Elektrolytverhältnis 0,005 Mol/l bis 3 Mol/l und die angelegte Gleichspannung 10 V bis 30 V beträgt.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass der Temperungsschritt 60 bis 240 Minuten bei einer Temperatur zwischen 350°C und 550°C und einem Druck zwischen 1 mbar und 10 mbar (zwischen 0,1 kPa und 1 kPa) stattfindet.

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

(i) Bereitstellen einer nach dem Verfahren nach einem der vorstehenden Ansprüche hergestellten lithografischen
5. Ein durch die nachstehenden Schritte gekennzeichnetes lithografisches Druckverfahren:

(i) Bereitstellen einer lithografischen Druckplatte nach dem in Anspruch 4 definierten Verfahren,
(ii) Herstellung mehrerer gedruckter Kopien durch Auftrag von Druckfarbe auf die Druckplatte und Übertragung der Druckfarbe auf Papier,
(iii) gegebenenfalls Reinigung der Druckplatte durch Entfernung der Druckfarbe von der Platte,
(iv) Löschen des lithografischen Bildes durch Flußbelichtung der Druckplatte mit UV-Licht, wobei hydrophobe Bereiche der Oberfläche hydrophil gemacht werden, und
(v) Wiederverwendung der so erhaltenen Vorstufe in einem nächsten, die Schritte (i) bis (iv) umfassenden Zyklus.

Revendications

1. Un procédé pour la fabrication d'un précurseur de plaque d'impression lithographique thermosensible à effet négatif, ledit procédé comprenant les étapes ci-après :

(i) la mise à disposition d'un support ayant une surface contenant du titane,
(ii) la modification de la surface en produisant un oxyde de titane hydrophile, ce processus consistant à :

1) anodiser la surface et
2) à tremper la surface anodisée sous pression réduite, l'oxyde de titane hydrophile pouvant être rendu hydrophobe par chauffage et/ou par exposition à des rayons infrarouges.

2. Procédé selon la revendication 1, caractérisé en ce que l'étape d'anodisation comprend le traitement de la surface à température ambiante dans une solution électrolytique aqueuse, la durée de l'électrolyse étant comprise entre 1 minute et 8 minutes, le rapport de l'électrolyte étant compris entre 0,005 mole/l et 3 moles/l et la tension continue appliquée étant comprise entre 10 V et 30 V.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'étape de trempage dure de 60 à 240 minutes à une température comprise entre 350°C et 550°C et sous une pression comprise entre 1 mbar et 10 mbars (entre 0,1 kPa et 1 kPa).

4. Un procédé pour la fabrication d'une plaque d'impression lithographique, ledit procédé comprenant les étapes ci-après :

(i) la mise à disposition d'un précurseur de plaque d'impression lithographique obtenu selon le procédé défini dans l'une quelconque des revendications précédentes,
(ii) le chauffage et/ou l'exposition à des rayons infrarouges sous forme d'image du précurseur, rendant hydrophobe la surface hydrophile dans des zones exposées du précurseur et assurant la formation d'une image lithographique sur la surface.

5. Un procédé d'impression lithographique comprenant les étapes ci-après :

(i) la mise à disposition d'une plaque d'impression lithographique selon le procédé défini dans la revendication 4,
(ii) la production d'une multitude de copies par encrage de la plaque d'impression et par transfert subséquent de l'encre sur du papier,
(iii) le nettoyage éventuel de la plaque d'impression en enlevant l'encre d'impression de la plaque,
(iv) l'effacement de l'image lithographique par exposition de la plaque d'impression au rayonnement d'un projecteur ultraviolet, hydrophiliisant ainsi des zones hydrophobes de la surface, et
(iv) la réutilisation du précurseur ainsi obtenu dans un cycle suivant comprenant les étapes (i) à (iv).
REFERENCES CITED IN THE DESCRIPTION

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