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(54) Method for making positive working lithographic printing plates

(57) According to the present invention there is provided a method for making positive working lithographic printing plates comprising the image-wise exposure of a heat-sensitive imaging element with an infrared laser and developing said imaging element in a simple wet clean-out process. The imaging element is exposed on an internal or flatbed scanner with a laser having a pixel dwell time of less than 0.2μs to obtain a positive working printing plate having a high sensitivity.

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Description

1. Field of the invention.

The present invention relates to a method for making lithographic printing plates involving the use of a heat-sensitive imaging element. More in particular the present invention relates to a method wherein the heat-sensitive imaging element is exposed to an infrared laser having a pixel dwell time of less than 0.075μs to obtain positive working printing plates with a high sensitivity.

2. Background of the invention.

Lithographic printing is the process of printing from specially prepared surfaces, some areas of which are capable of accepting ink, whereas other areas will not accept ink.

In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy ink in the photo-exposed (negative working) or in the non-exposed areas (positive working) on an ink-repelling background.

In the production of common lithographic 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.

Upon imagewise exposure of such 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.

On the other hand, 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 day light. Furthermore they have a problem of stability of sensitivity in view of the storage time and conditions. The trend towards heat-sensitive printing plate precursors is clearly seen on the market.

For example, Research Disclosure no. 33303 of January 1992 discloses a heat-sensitive 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.

US-P-4,708,925 discloses an imaging element including a photo-sensitive composition comprising an alkali-soluble novolac resin and an onium-salt. This composition can optionally contain an IR-sensitizer. After image-wise exposing said imaging element to UV - visible - or IR-radiation followed by a development step with an aqueous alkali liquid there is obtained a positive or negative working printing plate.

EP-A-625728 discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which can be positive or negative working. This layer comprises a resole resin,a novolac resin, a latent Bronsted acid and an IR-absorbing substance.

EP-A-738930 discloses an image-forming element comprising a substrate, and an image-forming medium comprising (a) a compound absorbing at a first wavelenght in the UV/blue region and (b) a dye absorbing at a second wavelenght which is longer than the first wavelenght, irradiation at said second wavelenght bleaching absorption of said compound (a) at said first wavelenght.suitable exposure dwell times are from about 1 μs to about 0.1 μs.

GB-1492070 discloses a planographic printing plate comprising a layer of material which is sensitive to ultraviolet light and overlying said layer, a second layer which is opaque to ultraviolet light and capable of being removed or rendered transparent to ultraviolet light by non-UV laser radiation.

EP-A-464270 discloses a method for writing characters on a tape or plate provided with radiation-sensitive portions, wherein the characters are written thereon by means of laser radiation, wherein after developing radiation -sensitive portions of the tape a protective layer is applied over at least the portions of the tape to be written on, the characters to be arranged are written onto the protective layerusing the laser beam, and that the material of the radiation-sensitive portions under the parts of the protective layer that has been written on are removed.

FR-1561957 discloses an imaging elementcomprising a photosensitive layer containing a binder and a liquid and/or solid material dispersed in said binder, said liquid and/or solid material being more hydrophobic than the binder.

EP-A-580394 discloses different kind of imaging apparatuses based on the use of lasers as exposing units.

The above discussed heat-sensitive imaging systems can be imaged with rotating drum image setters using one or more laser beams (resp. internal or external drum scanners). A disadvantage is that the sensitivity is not always satisfactory especially when internal drum scanners are used.

3. Summary of the invention.

It is an object of the present invention to provide a method for making positive working lithographic printing plates having excellent printing properties, developable in a convenient ecological way.

It is further an object of the present invention to provide a method for making positive working lithographic printing plates with improved sensitivity, imageable on an internal drum scanner.

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

According to the present invention there is provided a method for making high sensitive lithographic printing plates comprising the steps of image-wise exposing a heat-sensitive imaging element comprising on a lithographic base with a hydrophilic surface an hydrophobic infrared radiation sensitive layer and, without any further treatment except a thermal treatment, developing said imaging element in an aqueous alkaline solution, characterised in that the infrared laser has a pixel dwell time of less than 0.075μs.

Furthermore for use in the present invention there is provided a heat-sensitive imaging element comprising on a lithographic base an infrared radiation sensitive layer that can be partially or fully removed by exposure.

After the exposure the heat-sensitive imaging element is developed in a simple wet clean-out process by rinsing it with an aqueous alkaline solution.

4. Detailed description of the invention.

It has been found that according to the present invention, using a heat-sensitive imaging element as described above, positive working lithographic printing plates of high quality with improved sensitivity can be obtained by exposing said imaging element with an infrared laser having a pixel dwell time of less than 0.075μs, preferably of not more than 0.05μs. Said printing plates are obtained in an ecologically acceptable way.

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

As imaging apparatus for the image-wise laser exposure of the heat-sensitive imaging element an internal drum or flatbed scanner is used whereby the imaging element is exposed with one or a few laser beams having a short pixel dwell time (0.01μs to 0.07μs).

The infrared radiation sensitive layer comprises an infrared absorbing compound and a binder resin. Particularly useful infrared absorbing compounds are for example infrared dyes, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. $WO_{2.9}$. Preferably carbon black is used as the IR-absorbing compound. As a binder resin cellulose and its derivatives, cellulose esters e.g. cellulose acetate, cellulose nitrate etc., a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, phenolic resins e.g. phenol formaldehyde, cresol formaldehyde, novolac etc., polyesters (aromatic or aliphatic), polystyrenes, polycarbonates e.g. bisphenol A containing polycarbonates and copolymers or terpolymers of the above can be used.

Between the infrared sensitive layer and the lithographic base the present invention may comprise a thermally hardenable layer, comprising a self hardening hydrophobic polymer or a hardener and a hydrophobic polymerand being soluble in an aqueous developing solution more preferably an aqueous alkaline developing solution with preferentially a pH between 7.5 and 14. 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, polyvinyl phenols, carboxy substituted polymers etc. Typical examples of these polymers are descibed in DE-A-4007428, DE-A-4027301 and DE-A-4445820. The hydrophobic binder used in connection with the present invention is further characterised by: insolubility in water and partial solubility/swellability in an alkaline solution and/or partial solubility in water when combined with a cosolvent. Furthermore this aqueous alkali soluble layer is preferably a visible light- or UV-desensitised layer that is thermally hardenable and ink-accepting. This visible light- or 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.

According to one embodiment of the present invention, the lithographic base can be an anodised aluminum. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. According to the present invention, an 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 a sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. It is further evident that one or more of these post treatments may be carried out alone or in combination.

According to another embodiment in connection with the present invention, the lithographic base 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 crosslinking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetra-alkylorthosilicate. The latter is particularly preferred.

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.

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, preferably between 0.5 and 5 parts by weight, more preferably between 1.0 parts by weight and 3 parts by weight.

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 can 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.

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.

Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in EP-A 601240, GB-P-1419512, FR-P-2300354, US-P-3971660, US-P-4284705 and EP-A 514490.

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.

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 619524, EP-A 620502 and EP-A 619525. 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.

After the image-wise exposure the heat-sensitive imaging element is, without any additional treatment except a thermal treatment, developed by rinsing it with an aqueous alkaline developing solution. This development is a simple clean-out process whereby developing solutions with a pH between 7.5 and 14 such as the developing solutions that are used for developing conventional positive or negative working presensitised printing plates are employed. No additional pre-processing steps such as pre-baking are performed.

After the wet development of the 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 250°C for a period of 5 minutes to 1 minute.

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

EXAMPLES

Example 1: Positive working thermal plate which is imageable with pixel times <0.075μs

<u>Preparation of the lithographic printing plate</u>

On an Ozasol N61 printing plate (negative working printing plate from AGFA) was coated an IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	579.7
Butylacetate	386.5
Special Schwarz 250 (carbon black available from Degussa)	16.7
Nitrocellulose E950 (available from Wolff Walsrode)	12.3
Solsperse 5000 (wetting agent available from ICI)	0.3
Solsperse 28000 (wetting agent available from ICI)	1.7
Cymel 301 (melamine hardener available from Dyno Cyanamid)	2.3
p-toluene sulfonic acid	0.5

The UV-sensitive layer of the Ozasol N61 printing plate was coated by means of a knife coater with the IR-sensitive formulation to a wet coating thickness of 20 μm

Exposure with pixel time <0.075μs

The IR-sensitive printing plate was subjected to a scannnig Nd YAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05μs, spot size 14 μm and the power on the surface of the imaging element was varied from 2 to 6W). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EN143 (developing solution available from AGFA) hereby removing the IR-imaged parts and resulting in a positive printing plate. The sensitivity measured was 60mJ/cm^2.
After processing, the printing plate was mounted on a GTO46 offset-press. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

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

IR-laser exposure with short pixel dwell time(0.05μs)

Preparation of the lithographic base

A 0.20 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 to form a surface topography with an average center-line roughness Ra of 0.5 μm.
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 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 20 g/l of sodium bicarbonate at 40°C for 30 seconds, subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the imaging element

On a lithographic base was first coated a 5 % by weight solution of MARUKA LYNCUR M H-2 (homopolymer of polyvinylphenol from Maruzen Co.) in methyl ethyl ketone to a wet thickness of 20 μm. This layer was dried for 10 minutes at 40°C.
Upon this layer was then coated, with a wet coating thickness of 20μm, the IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	579.7
Butylacetate	386.5
Special Schwarz 250 (carbon black available from Degussa)	16.7
Nitrocellulose E950 (available from Wolff Walsrode)	12.3
Solsperse 5000 (wetting agent available from ICI)	0.3
Solsperse 28000 (wetting agent available from ICI)	1.7
Cymel 301 (melamine hardener available from Dyno Cyanamid)	2.3
p-toluene sulfonic acid	0.5

The IR-sensitive coating was dried for 2 minutes at 120°C.

<u>Imagewise exposure and processing of the imaging element</u>

The IR-sensitive printing plate was subjected to a scannig NdYAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05µs, spot size 14 µm and the power on the surface of the imaging element was varied from 2 Watts to 6 Watts). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (developing solution available fron AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate. The sensitivity measured was 45mJ/cm^2.
After processing, the printing plate was mounted on a GTO46 offset-press. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

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

IR-laser exposure with long pixel dwell time (0.1µs)

The imaging element of example 1 was subjected to a scanning NdYlf-laser emitting at 1050 nm (scanspeed 100 m/s, pixel time 0.1 µs , spot size 15 µm and the power on plate surface was varied from 75 to 475 mW). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (developing solution available from AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate. The sensitivity measured was 110mJ/cm^2.
After processing, the printing plate was mounted on a GTO46 offset-press. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.
So, it is seen that the sensitivity of the heat-sensitive imaging element is clearly lowered when the laser exposure is carried out at a dwell time longer than 0.075 µs.

Claims

1. A method for making high sensitive lithographic printing plates comprising the steps of image-wise exposing with a laser a positive heat-sensitive imaging element comprising on a lithographic base with a hydrophilic surface a hydrophobic infrared radiation sensitive layer and, without any further treatment except a thermal treatment, developing said imaging element in an aqueous alkaline developing solution, characterised in that the infrared laser has a pixel dwell time of less than 0.075µs.

2. A method according to claim 1 wherein said heat-sensitive imaging element is exposed on an internal drum or a flatbed scanner.

3. A method according to any of claims 1 or 2 wherein said heat-sensitive imaging element is developed in a simple wet clean-out process by rinsing it with an aqueous alkaline developing solution.

4. A heat-sensitive imaging element comprising on a lithographic base at least an infrared sensitive layer comprising an IR-absorber and a binder resin.

5. A heat-sensitive imaging element according to claim 4 wherein said infrared sensitive layer is partially or fully removed by exposure.

6. A heat-sensitive imaging element according to any of claims 4 or 5 wherein said infrared sensitive layer comprises nitrocellulose.

7. A heat-sensitive imaging element according to any of claims 4 to 6 wherein said imaging element comprises a thermally hardenable layer comprising a self-hardening hydrophobic polymer or a hardener and a hydrophobic polymer.

8. A heat-sensitive imaging element according to claim 7 wherein said self-hardening hydrophobic polymer is a phenolic resin.

9. A heat-sensitive imaging element according to any of claims 7 or 8 wherein said thermally hardenable layer is a visible light or UV-desensitised layer.

10. A heat-sensitive imaging element according to any of claims 7 to 9 wherein said thermally hardenable layer is ink-accepting.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0433

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	EP 0 720 057 A (KONISHIROKU PHOTO IND) 3 July 1996 * page 33, line 35 - line 58 * * page 43, line 50 - page 44, line 10 * * page 47, line 29 - line 40 * * page 49, line 55 - page 50, line 22; claims 1,11; figure 1 * ---	4-10 1-3	B41C1/10
P,X, L	EP 0 803 771 A (AGFA GEVAERT NV) 29 October 1997 * page 8, line 1 - line 8 * * page 10, line 44; claims; example 2 * ---	1-8,10	
T	EP 0 839 647 A (AGFA GEVAERT NV) 6 May 1998 * page 6, line 32 - line 33 * -----		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
B41C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 July 1998	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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