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(54) Method for making lithographic printing plates allowing for the use of lower laser writing power

(57) According to the present invention there is provided a method for making lithographic printing plates comprising the image-wise exposure of a heat-sensitive imaging element comprising on a hydrophilic lithographic base an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and a compound capable of converting light into heat present in said image-forming layer or a layer adjacent thereto and developing said imaging element by rinsing it with plain water or an aqueous solution. To allow for the use of lower laser writing power the heat-sensitive imaging element is heated to a temperature between 35 °C and 60 °C while being exposed.

Description

1. Field of the invention.

The present invention relates to a method for making a lithographic printing plate involving the use of a heat-sensitive imaging element. More in particular the present invention relates to a method wherein a heat-sensitive imaging element is heated while being exposed to allow for the use of lower laser writing power and is developed by means of plain water or an aqueous solution.

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 a 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 the light. Furthermore they have a problem of stability of sensitivity in view of the storage time and they show a lower resolution. 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.

EP-A-514145 discloses a heat-sensitive imaging element including a coating comprising core-shell particles having a water insoluble heat softenable core component and a shell component which is soluble or swellable in aqueous alkaline medium. Red or infrared laser light directed image-wise at said imaging element causes selected particles to coalesce, at least partially, to form an image and the non-coalesced particles are then selectively removed by means of an aqueous alkaline developer. Afterwards a baking step is performed. However the printing endurance of a so obtained printing plate is low.

EP-A-599510 discloses a heat-sensitive imaging element which comprises a substrate coated with (i) a layer which comprises (1) a disperse phase comprising a water-insoluble heat softenable component A and (2) a binder or continuous phase consisting of a component B which is soluble or swellable in aqueous, preferably aqueous alkaline medium, at least one of components A and B including a reactive group or precursor therefor, such that insolubilisation of the layer occurs at elevated temperature and/or on exposure to actinic radiation , and (ii) a substance capable of strongly absorbing radiation and transferring the energy thus obtained as heat to the disperse phase so that at least partial coalescence of the coating occurs. After image-wise irradiation of the imaging element and developing the image-wise irradiated plate, said plate is heated and/or subjected to actinic irradiation to effect insolubilisation. However the printing endurance of a so obtained printing plate is low.

Furthermore EP-A 952022871.0, 952022872.8, 952022873.6 and 952022874.4 disclose a method for making a lithographic printing plate comprising the steps of (1) image-wise exposing to light a heat-sensitive imaging element comprising (i) on a hydrophilic surface of a lithographic base an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and (ii) a compound capable of converting light to heat, said compound being comprised in said image-forming layer or a layer adjacent thereto; (2) and developing a thus obtained image-wise exposed element by rinsing it with plain water.

Still further FR 1,561,957 discloses a method for making a lithographic printing plate comprising the steps of (1) image-wise exposing to light a heat-sensitive imaging element comprising on a support an image-forming layer comprising hydrophobic particles dispersed in a hydrophilic binder and (ii) a compound capable of converting light to heat; (2) and developing a thus obtained image-wise exposed element by rinsing. Said document discloses that the heat-sensitive imaging document can be warmed-up before or during the exposition to light. Said document does however not disclose the temperature range of said overall heating.

US 3,642,475 discloses a heat-sensitive element which can be warmed-up before or during the exposition to light. Said document does however also not disclose the temperature range of said overall heating.

The above discussed heat-sensitive recording systems are exposed with lasers with a high power output. There is still a need for a heat-sensitive recording system that can be imaged with a laser having a low power output and that yields printing plates with good or excellent printing properties.

3. Summary of the invention.

It is an object of the present invention to provide a method for making a lithographic printing plate 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 lithographic printing plates with an improved sensitivity that are imageable with reduced laser writing power.

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 a lithographic printing plate comprising the image-wise exposure of a heat-sensitive imaging element comprising on a support, having a hydrophilic surface, an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and a compound capable of converting light into heat present in said image-forming layer or in a layer adjacent thereto and developing said imaging element by rinsing it with plain water or an aqueous solution, characterised in that said imaging element is overall heated to a temperature between 35 °C and 60 °C while being exposed.

4. Detailed description of the invention.

It has been found that according to the present invention, using an imaging element as described above, lithographic printing plates of high quality with improved sensitivity, imageable with reduced laser writing power and of high printing endurance can be obtained when said imaging element is overall heated to a temperature between 35 °C and 60 °C while being exposed. Said printing plates are provided in an ecologically acceptable way.

Overall heating of imaging material is disclosed in US-P-3,833,441 but for a material with a totally different composition

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.

To allow recording with a laser with a lower writing power (40mW - 520mW) the imaging element according to the present invention is overall heated while being exposed to a temperature between 35°C and 60°C. The imaging element can be heated according to the present invention by overall exposure with a laser preferably with a low writing power or a large spotsize, an IR-lamp or by mounting the imaging element on a print cylinder of a printing press which will be heated while being exposed.

In the present invention a heat-sensitive imaging element is used comprising on a hydrophilic surface of a lithographic base an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder. The hydrophilic binder used in connection with the present invention is preferably not crosslinked or only slightly crosslinked. The imaging element further includes a compound capable of converting light into heat. This compound is comprised in the image-forming layer or a layer adjacent thereto.

According to one embodiment of the present invention the lithographic base can be aluminium e.g. electrochemically and/or mechanically grained and anodised aluminium.

According to another embodiment in connection with the present invention, the lithographic base can comprise a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked rough hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or preferably a hydrolysed tetra-alkylorthosilicate.

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.

A cross-linked hydrophilic layer on a flexible support used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer e.g. colloidal silica. 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. Incorporation of these particles gives the surface of the cross-linked hydrophilic layer a uniform rough texture consisting of microscopic hills and valleys.

The thickness of the cross-linked hydrophilic layer 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 crosslinked hydrophilic layer 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.

Optionally, there may be provided one or more intermediate layers between the hydrophilic support and the image-forming layer. An image-forming layer in connection with the present invention comprises thermoplastic polymer particles dispersed in a hydrophilic binder.

Suitable hydrophilic binders for use in an image-forming layer in connection with this invention are water soluble (co)polymers for example synthetic homo- or copolymers such as polyvinylalcohol, a poly(meth)acrylic acid, a poly(meth)acrylamide, a polyhydroxyethyl(meth)acrylate, a polyvinylmethylether or natural binders such as gelatin, a polysaccharide such as e.g. dextran, pullulan, cellulose, arabic gum, alginic acid.

The hydrophilic binder can also be a water insoluble, alkali soluble or swellable resin having phenolic hydroxy groups and/or carboxyl groups.

Preferably the water insoluble, alkali soluble or swellable resin used in connection with the present invention comprises phenolic hydroxy groups. Suitable water insoluble, alkali soluble or swellable resins for use in an image-forming layer in connection with this invention are for example synthetic novolac resins such as ALNOVOL, a registered trade mark of Reichold Hoechst and DUREZ, a registered trade mark of OxyChem and synthetic polyvinylfenols such as MARUKA LYNCUR M, a registered trade mark of Dyno Cyanamid.

The hydrophilic binder used in connection with the present invention is preferably not cross-linked or only slightly cross-linked.

The thermoplastic polymer particles preferred in the embodiment of this invention are hydrophobic polymer particles. The hydrophobic thermoplastic polymer particles used in connection with the present invention have a coagulation temperature above 65°C and more preferably above 70°C. Coagulation may result from softening or melting of the thermoplastic polymer particles under the influence of heat. There is no specific upper limit to the coagulation temperature of the thermoplastic hydrophobic polymer particles, however the temperature should be sufficiently below the decomposition temperature of the polymer particles. Preferably the coagulation temperature is at least 10°C below the temperature at which the decomposition of the polymer particles occurs. When said polymer particles are subjected to a temperature above coagulation temperature they coagulate to form a hydrophobic agglomerate in the hydrophilic layer so that at these parts the hydrophilic layer becomes insoluble in plain water or an aqueous liquid. The temperature at which the imaging element is overall heated during exposure is below the coagulation temperature of the thermoplastic polymer particles.

Specific examples of hydrophobic polymer particles for use in connection with the present invention with a Tg above 80°C are e.g. polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile, polyvinyl carbazole etc. or copolymers thereof. Most preferably used are polystyrene, polymethyl-(meth)acrylate or copolymers thereof.

The weight average molecular weight of the polymers may range from 5,000 to 1,000,000g/mol.

The hydrophobic particles may have a particle size from 0.01 µm to 50 µm, more preferably between 0.05 µm and 10 µm and most preferably between 0.05 µm and 2 µm.

The polymer particles are present as a dispersion in the aqueous coating liquid of the image-forming layer and may be prepared by the methods disclosed in US-P-3,476,937. Another method especially suitable for preparing an aqueous dispersion of the thermoplastic polymer particles comprises:

- dissolving the hydrophobic thermoplastic polymer in an organic water immiscible solvent,
- dispersing the thus obtained solution in water or in an aqueous medium and
- removing the organic solvent by evaporation.

The amount of hydrophobic thermoplastic polymer particles contained in the image-forming layer is preferably at least 30% by weight and more preferably at least 45% by weight and most preferably at least 60% by weight.

The image-forming layer can also comprise crosslinking agents although this is not necessary. Preferred crosslinking agents are low molecular weight substances comprising a methylol group such as for example melamine-formaldehyde resins, glycoluril-formaldehyde resins, thiourea-formaldehyde resins, guanamine-formaldehyde resins, benzoguanamine-formaldehyde resins. A number of said melamine-formaldehyde resins and glycoluril-formaldehyde resins are commercially available under the trade names of CYMEL (Dyno Cyanamid Co., Ltd.) and NIKALAC (Sanwa Chemical Co., Ltd.).

The imaging element further includes a compound capable of converting light to heat. This compound is preferably comprised in the image-forming layer but can also be provided in a layer adjacent to the image-forming layer. Suitable compounds capable of converting light into heat are preferably infrared absorbing components although the wavelength of absorption is not of particular importance as long as the absorption of the compound used is 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, 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. $WO_{2.9}$. 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 results.

A light-to-heat converting compound in connection with the present invention is most preferably added to the image-forming layer but at least part of the light-to-heat converting compound may also be comprised in a neighbouring layer.

According to a method in connection with the present invention for obtaining a printing plate, the imaging element is image-wise exposed and subsequently developed by rinsing it with plain water before mounting the imaging element on the printing press.

In accordance with an alternative method of the present invention the imaging element is developed after the imaging element is exposed and mounted on the printing press.

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 can be developed by wiping the image-forming layer with e.g. a cotton pad or sponge soaked with water to remove the non-image forming areas.

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" , 15, 1995, page 4 to 6.

EP-A-664,211 discloses the use of a seamless offset printing member in a method of imaging a printing member. The composition of the imaging element is however totally different from the composition of the heat-sensiyive composition according to the invention

After the development of an image-wise exposed imaging element with an aqueous solution and drying the obtained plate can be used as a printing plate as such. However, it is still possible to bake said plate at a temperature between 100°C and 330°C for a period of 10 minutes to 1 minute. For example the exposed and developed plates can be baked at a temperature of 235°C for 2 minutes, at a temperature of 200°C for 5 minutes or at a temperature of 120°C for 10 minutes.

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

EXAMPLE

Preparation of a lithographic base:

To 700g of a dispersion containing 21.5% TiO_2 (average particle size 0.3 to 0.5µm) and 2.5% polyvinyl alcohol in deionised water were added, while stirring, 167g of a hydrolysed 22% tetramethylorthosilicate emulsion in water and 12g of a 10% solution of a wetting agent.

The obtained dispersion was coated on a 175µm polyethyleneterephtalate film support (coated with a hydrophilic adhesion layer) to a wet coating thickness of 50g/m^2, dried at 30°C and subsequently hardened by subjecting it to a temperature of 57°C for 1 week.

Preparation of the coating composition:

To 87.5g of a 20% dispersion of polystyrene (particle diameter of 63µm) stabilised with HOSTAPAL B (1.5% vs. polymer, HOSTAPAL is available from Hoechst) in deionised water was subsequently added while stirring, 16.7g of a 15% dispersion of carbon black containing a wetting agent in water, 785.8g of water, 100g of a 5% solution of 98% hydrolised polyvinyl acetate, having an average molecular weight of 200.000g/mol (MOWIOL 56-98 available from Hoechst) in water and 10.0g of a 10% solution of a wetting agent.

Preparation of the imaging element:

An imaging element for use according to the invention was produced by preparing the above coating composition for the infrared recording layer, and coating it onto the above prepared lithographic base in an amount of 30g/m^2 (wet coating amount) and drying it at 30°C.

Preparation of a printing plate:

An imaging element as described above was subjected to a scanning exposure with an infrared laser diode emitting at 830nm. During exposure the plate was overall heated as specified herinafter. Then it was developed with OZASOL EN220 (plate developing solution available from Hoechst). Printing plates were prepared according to the following conditions:

Test 1: Exposure at 830nm with a scanspeed of 1.1 m/s, a varying power output (30, 40, 50, 60 and 70mW on the image plane) and a spotsize of 9.6µ.
Overall heating at two different temperatures (24°C or 40°C)

Test 2: Exposure at 830nm with a scanspeed of 2.2 m/s, a varying power output (30, 40, 50, 60 and 70mW on the image plane) and a spotsize of 9.6µ.
Overall heating at two different temperatures (24°C or 40°C)

After development the line width was measured. The results of the respective tests are listed below in table 1.

TABLE 1

Scanspeed ⇒	Test 1 1.1 m/s		Test 2 2.2 m/s	
Power on the plate ⇓	24°C	40°C	24°C	40°C
30 mW	6.5µ	7.4µ	X	X
40 mW	7.4µ	10.2µ	X	5.6µ
50 mW	8.4µ	13.0µ	6.5µ	8.4µ
60 mW	9.3µ	15.8µ	7.4µ	11.2µ
70 mW	11.2µ	18.6µ	8.4µ	13.0µ
X: line width not measurable				

From the above results the laser energy needed on the image plane to form an image (J/m^2) was calculated (table 2).

TABLE 2

	24°C	40°C
Test 1: 1.1 m/s	2312 J/m^2	1549 J/m^2
Test 2: 2.2 m/s	1704 J/m^2	1174 J/m^2

As apparent from the results in table 1 and table 2 the heat-sensitive material can be recorded with less laser energy on the image plane and thus with a lower laser writing power to form an image when heated at 40 °C while being exposed.

Claims

1. A method for making a lithographic printing plate comprising the steps of image-wise exposing of a heat-sensitive imaging element comprising on a hydrophilic surface of a lithographic base an image-forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder and a compound capable of converting light into heat present in said image-forming layer or a layer adjacent thereto and developing said imaging element by rinsing it with plain water or an aqueous solution, characterised in that said image-forming material is overall heated to a temperature between 35 °C and 60 °C while being exposed.

2. A method according to claim 1 wherein said imaging element is image-wise exposed by means of an infrared laser or a plurality of infrared lasers.

3. A method according to claim 1 or 2 wherein said hydrophilic binder is a water soluble or swellable (co)polymer.

4. A method according to any of claims 1 to 3 wherein said hydrophobic thermoplastic polymer particles have a coagulation temperature of at least 65°C and wherein said temperature used for the overall heating of the imaging element during exposure is below the coagulation temperature of the thermoplastic polymer particles.

5. A method according to any of claims 1 to 4 wherein said lithographic base is anodised aluminium or comprises a flexible support having thereon a crosslinked hydrophilic layer.

6. A method for obtaining a lithographic printing plate according to any of claims 1 to 5 comprising the steps of developing the exposed imaging element by wiping it with water or an aqueous solution and mounting the exposed imaging element before or after development on the print cylinder of a printing press.

7. A method for obtaining a lithographic printing plate according to any of claims 1 to 6 wherein said lithographic printing plate formed is capable of being used as a seamless sleeve printing plate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 3130

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)
D,Y	FR 1 561 957 A (GEVAERT-AGFA) 4 April 1969 * page 7, right-hand column, line 34 - line 56; claims; example 12 * ---	1-7	B41C1/10 B41M5/36
Y,D	US 3 642 475 A (VRANCKEN MARCEL NICOLAS ET AL) 15 February 1972 * column 3, line 74 - column 4, line 5; claims * ---	1-7	
Y,D	EP 0 664 211 A (PRESSTEK INC) 26 July 1995 * claims * ---	7	
Y	US 3 833 441 A (R.B.HEIART) * column 4, line 24 - line 32 * ---	1	
Y,D	US 3 476 937 A (VRANCKEN MARCEL NICOLAS) * column 7, line 41 - line 43; claim 1 * -----	1,4	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B41C
B41M
B41N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 February 1998	Philosoph, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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