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

(57) According to the present invention there is provided a method for making lithographic printing plates including the following steps

a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing SiO_2 as silicate;
b) exposing imagewise said heat mode imaging element to IR-radiation;
c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for preparing a lithographic printing plate using a heat mode imaging element comprising an IR sensitive top layer.

[0002] More specifically the invention is related to a method for preparing a lithographic printing plate using a heat mode imaging element whereby the capacity of the top layer of being penetrated and/or solubilised by an aqueous developer is changed upon exposure.

BACKGROUND OF THE INVENTION

[0003] Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

[0004] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophilic background.

[0005] In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.

[0006] Upon imagewise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

[0007] Alternatively, printing plates are known that include a photosensitive coating that upon image-wise exposure is rendered soluble at the exposed areas. Subsequent development then removes the exposed areas. A typical example of such photosensitive coating is a quinone-diazide based coating.

[0008] Typically, the above described photographic materials from which the printing plates are made are camera-exposed through a photographic film that contains the image that is to be reproduced in a lithographic printing process. Such method of working is cumbersome and labor intensive. However, on the other hand, the printing plates thus obtained are of superior lithographic quality.

[0009] Attempts have thus been made to eliminate the need for a photographic film in the above process and in particular to obtain a printing plate directly from computer data representing the image to be reproduced. However the photosensitive coating is not sensitive enough to be directly exposed with a laser. Therefor it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide can then directly be exposed by means of a laser under the control of a computer. Subsequently, the silver halide layer is developed leaving a silver image on top of the photosensitive coating. That silver image then serves as a mask in an overall exposure of the photosensitive coating. After the overall exposure the silver image is removed and the photosensitive coating is developed. Such method is disclosed in for example **JP-A- 60- 61 752** but has the disadvantage that a complex development and associated developing liquids are needed.

[0010] **GB-1 492 070** discloses a method wherein a metal layer or a layer containing carbon black is provided on a photosensitive coating. This metal layer is then ablated by means of a laser so that an image mask on the photosensitive layer is obtained. The photosensitive layer is then overall exposed by UV-light through the image mask. After removal of the image mask, the photosensitive layer is developed to obtain a printing plate. This method however still has the disadvantage that the image mask has to be removed prior to development of the photosensitive layer by a cumbersome processing.

[0011] Furthermore methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat mode printing plate precursors is clearly seen on the market.

[0012] For example, **Research Disclosure no. 33303** of January 1992 discloses a heat mode imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink-acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.

[0013] **US-P- 4 708 925** discloses imaging elements including a photosensitive 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. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0014] **EP-A- 625 728** 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. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0015] **US-P- 5 340 699** is almost identical with **EP-A- 625 728** but discloses the method for obtaining a negative working IR-laser recording imaging element. The IR-sensitive layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0016] Furthermore **EP-A- 678 380** discloses a method wherein a protective layer is provided on a grained metal support underlying a laser-ablatable surface layer. Upon image-wise exposure the surface layer is fully ablated as well as some parts of the protective layer. The printing plate is then treated with a cleaning solution to remove the residu of the protective layer and thereby exposing the hydrophilic surface layer.

[0017] **EP-A- 97 200 588.8** discloses a heat mode imaging element for making lithographic printing plates comprising on a lithographic base having a hydrophilic surface an intermediate layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation wherein said top layer upon exposure to IR-radiation has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution. This material does not give a selective dissolution of the exposed or unexposed parts of the top and intermediate layer.

[0018] The above discussed systems have one or more disadvantages e.g. low infrared sensitivity, need for a preheating step (complex processing), are not imageable at short as well as at long pixel dwell times, lack a selective dissolution of the exposed or unexposed parts of the top and intermediate layer or said dissolution (development) is slow.

[0019] **GB-A- 1 155 035** discloses a method of recording information, wherein a recording material is used comprising a layer of a polymeric material which when any given area of the layer is sufficiently heated undergoes in that area a modification resulting in a decrease in the solubility of that area of the layer in water or an aqueous medium, such layer also incorporating a substance or substances distributed over the whole area of the layer and being capable of being heated by exposing the layer to intense radiant energy which is absorbed by such substance or substances, and wherein the said material is exposed to intense radiant energy which is distributed over the material in a pattern determined by the information to be recorded and which is at least partly absorbed by said distributed substance or substances, so that a corresponding heat pattern is generated in the material, whereby such information is recorded in terms of a difference in the solubilities in water or an aqueous medium of different areas of said layer.

[0020] **GB-A-1 245 924** discloses an information recording method wherein a recording material is used comprising a heat-sensitive recording layer of a composition such that the solubility of any given area of the layer in a given solvent can be increased by heating that area of the layer, wherein the said layer is information-wise heated to produce a record of the information in terms of a difference in the solubilities in the said solvent of different areas of the recording layer, and wherein the whole layer is then contacted with such solvent to cause the portions of the recording layer which are soluble or most soluble in such solvent to be removed or penetrated by such solvent.

[0021] **US-P- 5 466 557** discloses a radiation-sensitive composition comprising (1) a resole resin, (2) a novolac resin, (3) a latent Bronsted acid, (4) an infrared absorber, and (5) terephthalaldehyde.

[0022] **GB-A- 1 154 568** discloses a method of recording a graphic original having contrasting light-absorbing and light-transmitting areas, wherein a recording material comprising a supported layer composed mainly of gelatin the water-solubility or water-absorptive capacity of which increases if the layer is sufficiently heated , such layer also having light absorbing substance(s) distributed therein, is placed with such gelatin layer in contact with the light-absorbing areas of the original and the said gelatin layer is exposed to light through the original, the intensity of the light and the duration of the exposure being such that the areas of the gelatin layer in contact with the light-absorbing areas of the original are substantially unaffected by heat conduction from such light-absorbing areas, but the water-solubility or water-absorptive capacity of the other areas of the gelatin layer is increased by heating thereof due to absorption of copying light by the light-absorbing substance(s) in those other areas of the gelatin layer.

[0023] So there is still a need for heat mode imaging materials that can be imaged by laser exposure at short as well as at long pixel dwell times, need short development times and that yields lithographic printing plates with excellent printing properties.

OBJECTS OF THE INVENTION

[0024] It is an object of the invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element having excellent printing properties, developable in a selective, rapid convenient and ecological way.

[0025] It is further an object of the present invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element having a high infrared sensitivity.

[0026] It is also an object of the present invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element wich can be imaged by laser exposure at short as well as at long pixel dwell times.

[0027] Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION

[0028] According to the present invention there is provided a method for making lithographic printing plates including the following steps:

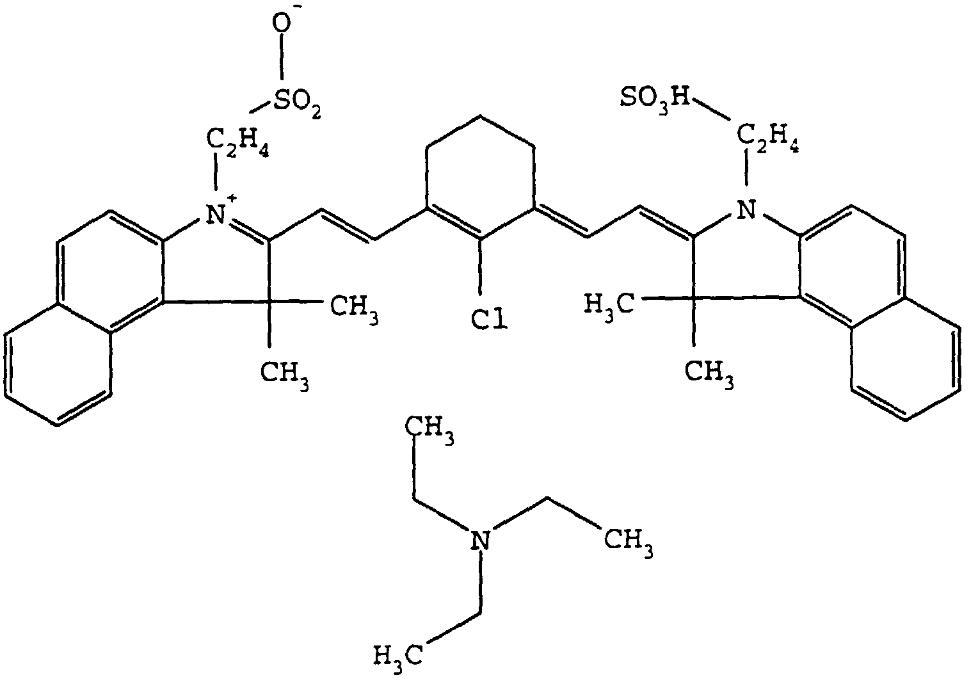
a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and which is unpenetrable for an alkaline developer containing SiO_2 as silicate;
b) exposing imagewise said heat mode imaging element to IR-radiation;
c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved, characterized in that said top layer includes an IR-dye.

DETAILED DESCRIPTION OF THE INVENTION

[0029] According to the present invention there is provided a method for making lithographic printing plates including the following steps:

a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and which is unpenetrable for an alkaline developer containing SiO_2;
b) exposing imagewise said heat mode imaging element to IR-radiation;
c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved, characterized in that said top layer includes an IR-dye.

[0030] The top layer, in accordance with the present invention comprises an IR-dye and a binder resin. A mixture of IR-dyes may be used, but it is preferred to use only one IR-dye. Preferably said IR-dyes are IR-cyanines dyes. Particularly useful IR-cyanine dyes are cyanines dyes with two acid groups, more preferably with two sulphonic groups . Still more preferably are cyanines dyes with two indolenine and two sulphonic acid groups. Most preferably is compound I with the structure as indicated



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[0031] The top layer can comprise as binder a water insoluble polymer such as such as a cellulose ester, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, silicone resins, etc.

[0032] The top layer comprises as a binder resin in accordance with the present invention preferably a water soluble polymer. As water soluble polymer a protein, preferably gelatin may be used. However, also synthetic, semi-synthetic, or natural water soluble polymers may be used. Synthetic polymers are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates. 650nm. In this way a daylight stable printing plate can be obtained.

[0033] Said first layer preferably also includes a low molecular acid, preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid.

[0034] The ratio between the total amount of low molecular acid and polymer in the first layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 20:80. The total amount of said first layer preferably ranges from 0.1 to 10 g/m^2, more preferably from 0.3 to 2 g/m^2.

[0035] In the imaging element according to the present invention, the lithographic base can be an anodised aluminum. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or 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. 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**.

[0036] According to another embodiment in connection with the present invention, the lithographic base having a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetraalkylorthosilicate. The latter is particularly preferred.

[0037] 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.

[0038] 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.

[0039] 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.

[0040] 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.

[0041] 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**.

[0042] 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.

[0043] It is particularly preferred to use a polyester film support to which an adhesion improving layer has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in **EP-A- 619 524**, **EP-A- 620 502** and **EP-A- 619 525**. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

[0044] Image-wise exposure in connection with the present invention is an image-wise scanning exposure involving the use of a laser that operates in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared. Exposure of the imaging element can be performed with lasers with a short as well as with lasers with a long pixel dwell time. Preferred are lasers with a pixel dwell time between 0.005 μs and 20 μs.

[0045] After the image-wise exposure the heat mode imaging element is developed by rinsing it with an aqueous alkaline solution. The aqueous alkaline solutions used in the present invention are preferably those that are used for developing conventional positive working presensitised printing plates and have preferably a pH between 11.5 and 14. Thus the imaged parts of the top layer that were rendered more penetrable for the aqueous alkaline solution upon exposure and the corresponding parts of the underlying layer are cleaned-out whereby a positive working printing plate is obtained.

[0046] In the present invention, the composition of the developer used is also very important.

[0047] Therefore, to perform development processing stably for a long time period particularly important are qualities such as strength of alkali and the presence of silicates in the developer. Under such circumstances, the present inventors have found that a rapid high temperature processing can be performed, that the amount of the replenisher to be supplemented is low and that a stable development processing can be performed over a long time period of the order of not less than 3 months without exchanging the developer only when the developer having the foregoing composition is used.

[0048] The developers and replenishers for developer used in the invention are preferably aqueous solutions mainly composed of alkali metal silicates and alkali metal hydroxides represented by MOH or their oxyde, represented by M_2O, wherein said developer comprises SiO_2 and M_2O in a molar ratio of 0.5 to 1.5 and a concentration of SiO_2 of 0.5 to 5% by weight.. As such alkali metal silicates, preferably used are, for instance, sodium silicate, potassium silicate, lithium silicate and sodium metasilicate. On the other hand, as such alkali metal hydroxides, preferred are sodium hydroxide, potassium hydroxide and lithium hydroxide.

[0049] The developers used in the invention may simultaneously contain other alkaline agents. Examples of such other alkaline agents include such inorganic alkaline agents as ammonium hydroxide, sodium tertiary phosphate, sodium secondary phosphate, potassium tertiary phosphate, potassium secondary phosphate, ammonium tertiary phosphate, ammonium secondary phosphate, sodium bicarbonate, sodium carbonate, potassium carbonate and ammonium carbonate; and such organic alkaline agents as mono-, di- or triethanolamine, mono-, di- or trimethylamine, mono-, di- or triethylamine, mono- or diisopropylamine, n-butylamine, mono-, di- or triisopropanolamine, ethyleneimine, ethylenediimine and tetramethylammonium hydroxide.

[0050] In the present invention, particularly important is the molar ratio in the developer of [SiO_2] / [M_2O], which is generally 0.5 to 1.5, preferably 0.7 to 1.3. This is because if the molar ratio is less than 0.5, great scattering of activity is observed, while if it exceeds 1.5, it becomes difficult to perform rapid development and the dissolving out or removal of the light-sensitive layer on non-image areas is liable to be incomplete. In addition, the concentration of SiO_2 in the developer and replenisher preferably ranges from 1 to 4 % by weight. Such limitation of the concentration of SiO_2 makes it possible to stably provide lithographic printing plates having good finishing qualities even when a large amount of plates according to the invention are processed for a long time period.

[0051] In a particular preferred embodiment, an aqueous solution of an alkali metal silicate having a molar ratio [SiO_2] / [M_2O], which ranges from 1.0 to 1.5 and a concentration of SiO_2 of 1 to 4 % by weight is used as a developer. In such case, it is a matter of course that a replenisher having alkali strength equal to or more than that of the developer is employed. In order to decrease the amount of the replenisher to be supplied, it is advantageous that a molar ratio, [SiO_2] / [M_2O], of the replenisher is equal to or smaller than that of the developer, or that a concentration of SiO_2 is high if the molar ratio of the developer is equal to that of the replenisher.

[0052] In the developers and the replenishers used in the invention, it is possible to simultaneously use organic solvents having solubility in water at 20 °C of not more than 10 % by weight according to need. Examples of such organic solvents are such carboxilic acid esters as ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, ethylene glycol monobutyl acetate, butyl lactate and butyl levulinate; such ketones as ethyl butyl ketone, methyl isobutyl ketone and cyclohexanone; such alcohols as ethylene glycol monobutyl ether, ethylene glycol benzyl ether, ethylene glycol monophenyl ether, benzyl alcohol, methylphenylcarbinol, n-amyl alcohol and methylamyl alcohol; such alkyl-substituted aromatic hydrocarbons as xylene; and such halogenated hydrocarbons as methylene dichloride and monochlorobenzene. These organic solvents may be used alone or in combination. Particularly preferred is benzyl alcohol in the invention. These organic solvents are added to the developer or replenisher therefor generally in an amount of not more than 5 % by weight and preferably not more than 4 % by weight.

[0053] The developers and replenishers used in the present invention may simultaneously contain a surfactant for the purpose of improving developing properties thereof. Examples of such surfactants include salts of higher alcohol (C8 ~ C22) sulfuric acid esters such as sodium salt of lauryl alcohol sulfate, sodium salt of octyl alcohol sulfate, ammonium salt of lauryl alcohol sulfate, Teepol B-81 (trade mark, available from Shell Chemicals Co., Ltd.) and disodium alkyl sulfates; salts of aliphatic alcohol phosphoric acid esters such as sodium salt of cetyl alcohol phosphate; alkyl aryl sulfonic acid salts such as sodium salt of dodecylbenzene sulfonate, sodium salt Of isopropylnaphthalene sulfonate,sodium salt of dinaphthalene disulfonate and sodium salt of metanitrobenzene sulfonate; sulfonic acid salts of alkylamides such as $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$ and sulfonic acid salts of dibasic aliphatic acid esters such as sodium dioctyl sulfosuccinate and sodium dihexyl sulfosuccinate. These surfactants may be used alone or in combination. Particularly preferred are sulfonic acid salts. These surfactants may be used in an amount of generally not more than 5 % by weight and preferably not more than 3 % by weight.

[0054] In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0055] Examples of such compounds are neutral salts such as NaCl, KCl and KBr as disclosed in **JN-A- 58- 75 152**; chelating agents such as EDTA and NTA as disclosed in **JN-A- 58- 190 952 (U.S-A- 4 469 776)**, complexes such as [Co(NH3)6]Cl3 as disclosed in **JN-A- 59- 121 336 (US-A- 4 606 995);** ionizable compounds of elements of the group IIa, IIIa or IIIb of the Periodic Table such as those disclosed in **JN-A- 55- 25 100**; anionic or amphoteric surfactants such as sodium alkyl naphthalene sulfonate and N-tetradecyl-N,N-dihydroxythyl betaine as disclosed in **JN-A- 50- 51 324**; tetramethyldecyne diol as disclosed in **US-A- 4 374 920**; non-ionic surfactants as disclosed in **JN-A- 60- 213 943**; cationic polymers such as methyl chloride quaternary products of p-dimethylaminomethyl polystyrene as disclosed in **JN-A- 55- 95 946**; amphoteric polyelectrolytes such as copolymer of vinylbenzyl trimethylammonium chloride and sodium acrylate as disclosed in **JN-A- 56- 142 528**; reducing inorganic salts such as sodium sulfite as disclosed in **JN-A- 57- 192 952 (US-A- 4 467 027)** and alkaline-soluble mercapto compounds or thioether compounds such as thiosalicylic acid, cysteine and thioglycolic acid; inorganic lithium compounds such as lithium chloride as disclosed in **JN-A- 58- 59 444**; organic lithium compounds such as lithium benzoate as disclosed in **JN-A- 50 34 442**; organometallic surfactants containing Si, Ti or the like as disclosed in **JN-A- 59- 75 255**; organoboron compounds as disclosed in **JN-A- 59- 84 241 (US-A- 4 500 625)**; quaternary ammonium salts such as tetraalkylammonium oxides as disclosed in **EP-A- 101**

010; and bactericides such as sodium dehydroacetate as disclosed in **JN-A- 63- 226 657**.

In the method for development processing of the present invention, any known means of supplementing a replenisher for developer may be employed. Examples of such methods preferably used are a method for intermittently or continuously supplementing a replenisher as a function of the amount of PS plates processed and time as disclosed in **JN-A- 55- 115 039** (**GB-A- 2 046 931**), a method comprising disposing a sensor for detecting the degree of light-sensitive layer dissolved out in the middle portion of a developing zone and supplementing the replenisher in proportion to the detected degree of the light-sensitive layer dissolved out as disclosed in **JN-A- 58- 95 349** (**US-A- 4 537 496**); a method comprising determining the impedance value of a developer and processing the detected impedance value by a computer to perform supplementation of a replenisher as disclosed in **GB-A- 2 208 249**.

[0056] The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slided on the print cylinder instead of applying in a classical way a classically formed printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

[0057] After the development of an image-wise exposed imaging element with an aqueous alkaline solution and drying, the obtained plate can be used as a printing plate as such. However, to improve durability it is still possible to bake said plate at a temperature between 200°C and 300°C for a period of 30 seconds to 5 minutes. Also the imaging element can be subjected to an overall post-exposure to UV-radiation to harden the image in order to increase the run lenght of the printing plate.

[0058] 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 based on an alkali-soluble binder.

Preparation of the lithographic base

[0059] 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 mm.

[0060] 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.

[0061] The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m^2 for about 300 seconds to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3 then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and then with a solution containing aluminum trichloride, subsequently rinsed with demineralized water at 20°C during 120 seconds and died.

Preparation of the first layer.

[0062] To 740 g of tetrahydrofuran and 503 g of methoxypropanol was added a solution of 48 g alnovol in 74 g of methoxypropanol and 6.55g of 3,4,5-trimethoxybenzoic acid and said solution was coated on the anodized layer of the aluminum support at a wet thickness of 20 μm, giving a dry weight of 0.76 g/m^2.

Preparation of the top layer

[0063] On the first layer was coated a layer from an aqueous solution containing 0.06 g/m^2 of IR cyanine dye Cpd I and 0.54 g/m^2 polyacrylic acid (Carbopol WS 801 from Goodrich)

[0064] Next to the above described material I was prepared an identical material II with the exception that the top layer only contained 0.54 g/m^2 of polyacrylic acid and no IR cyanine dye

[0065] Both materials were imaged with an external drum IR-laser imaging apparatus (diode laser 830 nm, drum-speed 3.2 m/s, addressability 3600 dpi, power level in image plane 80-120 mW), and developed in an alkaline silicate containing developing solution (75% EP 26 developer commercially available from Agfa), containing 1.16 weight percent of SiO_2 and a molar ratio of [SiO_2] to [Na_2O] of 0.59.,dissolving very rapidly the exposed parts. With the material having no IR-cyanine cyanine dye in the toplayer the non exposed parts were also rapidly dissolved; a selective dissolution of the exposed parts was not possible. With the material I containing an IR cyanine cyanine dye a selective dissolution of the exposed parts was obtained.

[0066] At 2400 dpi images were obtained with material I using 80 mW power or more in imageplane. This plate was printed on a Heidelberg GTO 46 printing machine with a conventional ink (K+E197) and fountain solution (Rotamatic) resulting in good prints, i.e. no scumming in non imaged parts and good ink-uptake in imaged parts.

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

[0067] A heat mode material III was prepared in an identical way as material I except that the top layer contained 0.06 g/m^2 of Carbon black (trade name Printex L6) and 0.54 g/m^2 polyacrylic acid(Carbopol WS 801 from Goodrichg)

[0068] Materials I and III were imaged with an external drum IR-laser imaging apparatus (diode laser 830 nm, drumspeed 3.2 m/s, addressability 3600 dpi, power level in image plane 80-120 mW), and developed in an alkaline silicate containing developing solution (75% EP 26 developer commercially available from Agfa), containing 1.16 weight percent of SiO_2 and a molar ratio of [SiO_2] to [Na_2O] of 0.59 dissolving very rapidly the exposed parts. With the material having no IR-cyanine dye in the toplayer the non exposed parts were also rapidly dissolved; a selective dissolution of the exposed parts was not possible. With the material I containing an IR cyanine dye a selective dissolution of the exposed parts was obtained.

[0069] At 2400 dpi images were obtained with material I using 80 mW power or more in imageplane. This plate was printed on a Heidelberg GTO 46 printing machine with a conventional ink (K+E197) and fountain solution (Rotamatic) resulting in good prints, i.e. no scumming in non imaged parts and good ink-uptake in imaged parts.

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

[0070] On a lithographic base as described above is coated a first layer identical with the first layer of example 1 but at a concentration of 3% and at a wet coating thickness of 30 μm giving a dry weight of 0.90 g/m^2.

[0071] On the first layer was coated a layer from an aqueous solution containing 0.18 g/m^2 of IR cyanine dye Cpd I and 0.42 g/m^2 polyacrylic acid (Carbopol WS 801 from Goodrich)

[0072] This material was imaged with an external drum IR-laser imaging apparatus (diode laser 830 nm, drumdpeed 3.2 m/s, addressability 3600 dpi, power level in image plane 80-120 mW), and developed in an alkaline silicate containing developing solution (75% EP 26 developer commercially available from Agfa), containing 1.16 weight percent of SiO_2 and a molar ratio of [SiO_2] to [Na_2O] of 0.59.dissolving very rapidly the exposed parts. This plate was printed on a Heidelberg GTO 46 printing machine with a conventional ink (K+E197) and fountain solution (Rotamatic) resulting in good prints, i.e. no scumming in non imaged parts and good ink-uptake in imaged parts for more than 17,000 copies.

EXAMPLE 4 :Positive working thermal plate based on an alkali-soluble binder

[0073] On a lithographic base as described above is coated a first layer identical with the first layer of example 1.

[0074] On the first layer was coated a layer from an aqueous solution containing 0.09 g/m^2 of IR cyanine dye Cpd I and 0.51 g/m^2 gelatine.

[0075] This material was imaged with an external drum IR-laser imaging apparatus (diode laser 830 nm, drumdpeed 3.2 m/s, addressability 3600 dpi, power level in image plane 80-120 mW), and developed in an alkaline silicate containing developing solution (75% EP 26 developer commercially available from Agfa), containing 1.16 weight percent of SiO_2 and a molar ratio of [SiO_2] to [Na_2O] of 0.59.dissolving very rapidly the exposed parts. This plate was printed on a Heidelberg GTO 46 printing machine with a conventional ink (K+E197) and fountain solution (Rotamatic) resulting in good prints, i.e. no scumming in non imaged parts and good ink-uptake in imaged parts for more than 17,000 copies.

Claims

1. A method for making lithographic printing plates including the following steps

a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing SiO_2 as silicate;

b) exposing imagewise said heat mode imaging element to IR-radiation;

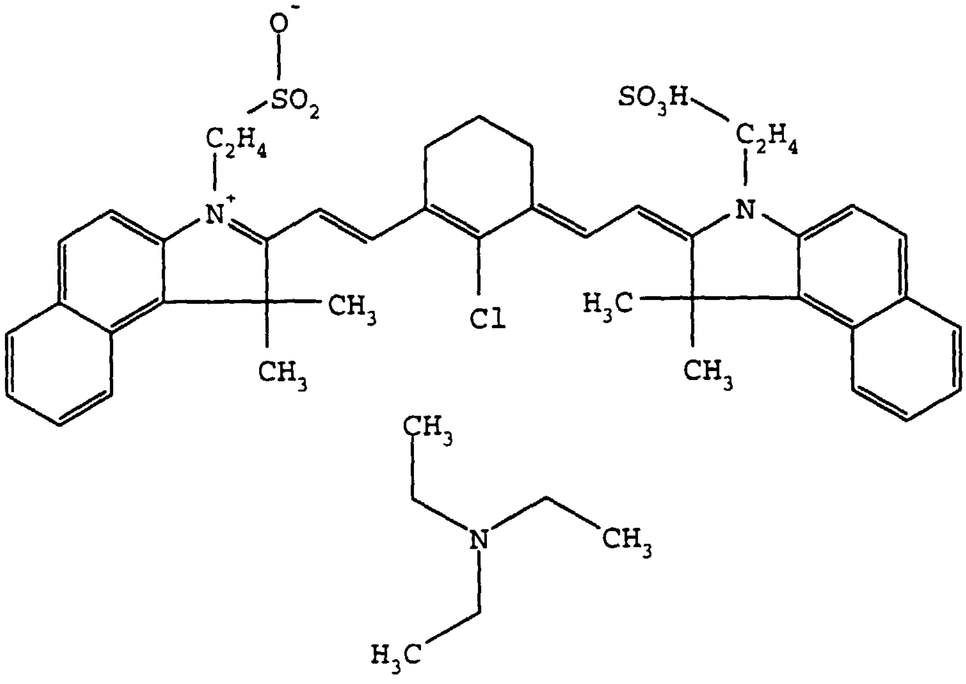
c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye.

2. A method for making lithographic printing plates according to claim 1 wherein said IR-dye is an IR-cyanine dye.

3. A method for making lithographic printing plates according to claim 2 wherein said IR-cyanine dye comprises two acid groups.

4. A method for making lithographic printing plates according to claim 3 wherein said infrared cyanine dye comprises two indolenine groups.

5. A method for making lithographic printing plates according to claim 4 wherein said infrared cyanine dye is compound I with the structure as indicated



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6. A method for making lithographic printing plates according to any of claims 1 to 5 wherein the polymer included in the top layer is a water soluble polymer.

7. A method for making lithographic printing plates according to claim 6 wherein said polymer comprises acidic groups.

8. A method for making lithographic printing plates according to claim 7 wherein said polymer is a compound selected from the group consisting of polymethacrylic acid and polyacrylic acid.

9. A method for making lithographic printing plates according to any of claims 1 to 8 wherein said alkaline developer comprises SiO_2 and M_2O in a molar ratio of 0.5 to 1.5 and a concentration of SiO_2 of 0.5 to 5% by weight.

10. A method for making lithographic printing plates according to claim 9 wherein said imagewise exposed heat mode imaging element is developed with an alkaline developer containing SiO_2 and M_2O in a molar ratio of 0.7 to 1.3.

11. A method for making lithographic printing plates according to claims 9 or 10 wherein said imagewise exposed heat mode imaging element is developed with an alkaline developer containing SiO_2 in the range from 1 to 4 % by weight.

12. A method for making lithographic printing plates according to any of claims 1 to 10 wherein the binder of the first layer is novolac.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 3120

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 Y	GB 1 155 035 A (GEVAERT-AGFA N.V.) 11 June 1969 * claim 10 * * page 2, line 42 - line 54 * * page 4, line 41 - line 47 * * page 3, line 27 * * page 2, line 18 - page 3, line 13 * ---	1-12 1	B41C1/10 B41M5/36
X	GB 1 245 924 A (AGFA-GEVAERT N.V.) 15 September 1971 * page 1, line 63 * * page 2, line 2 - line 10 * * page 2, line 72 - line 78 * * page 6, line 35 - line 53; example 8 * * page 5, line 33 - page 6, line 75 * ---	1-12	
Y Y	US 5 466 557 A (HALEY NEIL F ET AL) 14 November 1995 * column 10, line 48 - line 56; claim 1 * ---	1-12 1-12	
X	GB 1 154 568 A (AGFA-GEVAERT N.V.) 11 June 1969 * the whole document * ---	1	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** B41C B41M G03F
A	EP 0 732 628 A (MINNESOTA MINING & MFG) 18 September 1996 * the whole document * ---	1	
A	EP 0 347 245 A (FUJI PHOTO FILM CO LTD) 20 December 1989 * the whole document * ---	1	
A	GB 1 160 221 A (GEVAERT-AGFA N.V.) 6 August 1969 * the whole document * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 February 1999	Rasschaert, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 20 3120

15-02-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1155035 A	11-06-1969	NL 6608712 A	25-11-1966
GB 1245924 A	15-09-1971	BE 721468 A DE 1797415 A FR 1588977 A US 3628953 A	27-03-1969 19-08-1971 16-03-1970 21-12-1971
US 5466557 A	14-11-1995	NONE	
GB 1154568 A	11-06-1969	US 3811773 A BE 683054 A CH 477295 A NL 6608711 A	21-05-1974 27-11-1966 31-08-1969 25-11-1974
EP 0732628 A	18-09-1996	JP 8262742 A US 5670294 A	11-10-1996 23-09-1997
EP 0347245 A	20-12-1989	JP 2003065 A JP 2639693 B DE 68922144 D DE 68922144 T	08-01-1990 13-08-1997 18-05-1995 10-08-1995
GB 1160221 A	06-08-1969	AT 279350 B BE 681138 A CH 480189 A DE 1571816 A FR 1532243 A NL 6606719 A SE 338712 B US 3793025 A US 4004924 A	10-03-1970 17-11-1966 31-10-1969 14-01-1971 18-11-1968 25-10-1966 13-09-1971 19-02-1974 25-01-1977

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