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

(57) According to the present invention there is provided a heat mode imaging element for making a lithographic printing plate having on a lithographic base with a hydrophilic surface a first layer including a polymer that is soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer that is IR-sensitive and unpenetrable for an alkaline developer; characterized in that at least one of said first layer and said top layer comprises a surfactant.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a heat mode imaging element for preparing a lithographic printing plate. More specifically the invention is related to a heat mode imaging element for preparing a lithographic printing plate whereof the difference in the top layer of being penetrated and/or solubilised in the exposed areas and in the non-exposed areas by an aqueous developer is increased.

BACKGROUND OF THE INVENTION

[0002] 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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] 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.

[0007] 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.

[0008] 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 may 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.

[0009] **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.

[0010] 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.

[0011] 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.

[0012] **US-P- 4 708 925** discloses imaging elements including a photosensitive composition comprising an alkali-soluble novolac resin and an onium-salt. This composition may 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.

[0013] **EP-A- 625 728** discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which may 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.

[0014] **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.

[0015] **GB-A- 1 208 415** discloses a method of recording information comprising information-wise heating a recording material comprising a support bearing, with or without an interlayer a heat-sensitive recording layer constituted so that such information-wise heating creates a record of the information in terms of a difference in the water permeabilities of different areas of the recording layer, treating the recording material with an aqueous liquid which penetrates through the water-permeable or more water-permeable areas of the recording layer and is constituted so as to effect a permanent physical and/or chemical change of at least the surface portions of the underlying support or inter-layer in the corresponding areas, and removing the whole of the recording layer to expose said inforlmation-wise changed support or interlayer.

[0016] **JP-A-01-46739** discloses a method for preventing the line-like unequalities generated by foam by dissolving a photosensitive composition containing at least a photosensitive material, fluorine surfactant and defoaming agent into a coating solvent, then coating the solution on a base and drying the coating.

[0017] **JP-A-02-29750** discloses a method for obtaining a photosensitive composition suitable for a positive photosensitive printing plate by using o-naphthoquinonediazide sulphonic acid, an alkali-soluble resin, and a non-ionic surfactant such as polyoxyethylene naphthol.

[0018] **EP-A- 527.369** discloses a light sensitive recording material comprising a support and a positive working light sensitive layer with a rough surface, which comprises as light sensitive compound at least a 1,2-quinonediazide and as water insoluble and in water-alkaline solutions soluble or swellable binder a polycondensate or polymer and a filler, wherein the light-sensitive layer at a layer weight of 3g/m^2 or less (i) comprises as filler silica with a mean diameter from 3 to 5 μm and a final limit of 15 μm in an amount, which yields a slipperiness according to Beck from 20 till 100 seconds and (ii) furthermore comprises a surfactant with polysiloxane units.

[0019] **EP-A- 823 327** discloses a positive photosensitive composition showing a difference in solubility in an alkali developer as between an exposed portion and a non-exposed portion, which comprises, as components inducing the difference in solubility, (a) a photo-thermal conversion material, and (b) a high molecular compound, of which the solubility in an alkali developer is changeable mainly by a change other than a chemical change.

[0020] 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.

[0021] **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.

[0022] Said last heat-mode imaging element has the disadvantage that the difference between the solubility in the exposed areas and in the non-exposed aqreas is not very great so that also non-exposed areas are dissolved during the processing of said element so that said plates could not be used as lithographic plates.

OBJECTS OF THE INVENTION

[0023] It is an object of the invention to provide a heat mode imaging element for making in an easy way lithographic printing plates.

[0024] It is another object of the invention to provide a heat mode sensitive imaging element for making positive lithographic printing plates 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 heat mode sensitive imaging element having a high

infrared sensitivity.

[0026] It is also an object of the present invention to provide a heat mode sensitive imaging element wich has a great difference in developability in a developer between the exposed areas and the non-exposed areas.

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

SUMMARY OF THE INVENTION

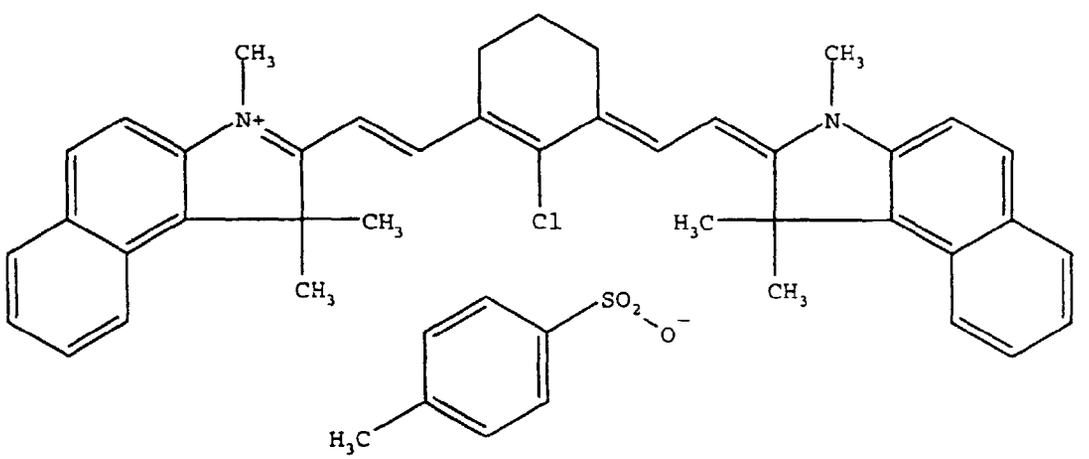
[0028] According to the present invention there is provided a heat mode imaging element for making a lithographic printing plate having on a lithographic base with a hydrophilic surface a first layer including a polymerthat is soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer that is IR-sensitive and unpenetrable for an alkaline developer; characterized in that at least one of said first layer and said top layer comprises a surfactant.

DETAILED DESCRIPTION OF THE INVENTION

[0029] It has been found that a heat-sensitive imaging element according to the invention can be obtained in an easy way, which yields a lithographic printing plate of high quality.

[0030] The first layer and/or the top (also called the second) layer comprises a surfactant. Said surfactant can be a cationic, an anionic or an amphoteric surfactant, but is preferably a non-ionic surfactant. The surfactant is preferably selected from the group consisting of perfluoroalkyl surfactants, alkylphenyl surfactants and most preferably polysiloxane surfactants. Still more preferably a combination of at least two polysiloxane surfactants is used. The surfactant is preferably present in the top layer. The amount of surfactant lies preferably in the range from 0.001 to 0.3g/m^2, more preferably in the range from 0.003 to 0.050g/m^2.

[0031] The top layer, in accordance with the present invention comprises an IR-dye or pigment and a binder resin. A mixture of IR-dyes or pigments may be used, but it is preferred to use only one IR-dye or pigment. Preferably said IR-dyes are IR-cyanines dyes. Particularly useful IR-cyanine dyes are cyanines dyes with two indolenine groups. Most preferably is compound I with the structure as indicated



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Particularly useful IR-absorbing pigments are 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. WO2.9. 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 and favorable results.

[0032] When said top layer contains an IR-dye, said top layer preferably also contains a dye or a pigment that absorbs in the visible region in order to be able to visually inspect the image formed after IR-radiation and development in an aqueous alkaline developer.

[0033] The IR-absorbing dyes or pigments are present preferably in an amount between 1 and 99 parts, more preferably between 50 and 95 parts by weight of the total amount of said IR-sensitive top layer.

[0034] The top layer may preferably comprise as binder a water insoluble polymer such as a cellulose ester, a co-

polymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, silicone resins, etc. Preferred as binder is nitrocellulose resin.

[0035] The total amount of the top layer preferably ranges from 0.010 to 5 g/m^2 more preferably from 0.020 to 1 g/m^2.

[0036] In the top layer a difference in the capacity of being penetrated and/or solubilised by the aqueous alkaline solution is generated upon image-wise exposure for an alkaline developer according to the invention.

[0037] In the present invention the said capacity is increased upon image-wise IR exposure to such degree that the imaged parts will be cleaned out during development without solubilising and/or damaging the non-imaged parts.

[0038] The development with the aqueous alkaline solution is preferably done within an interval of 5 to 120 seconds.

[0039] Between the top layer and the lithographic base the present invention comprises a first layer soluble in an aqueous developing solution, more preferably an aqueous alkaline developing solution with preferentially a pH between 7.5 and 14. Said layer is preferably contiguous to the top layer but other layers may be present between the top layer and the first layer. 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 resins, polymers containing hydroxystyrene units, carboxy substituted polymers etc. Typical examples of these polymers are descibed in **DE-A- 4 007 428, DE-A- 4 027 301** and **DE-A- 4 445 820**. 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.

[0040] Furthermore this aqueous alkali soluble layer is preferably a visible light- and UV-light desensitised layer. Said layer is preferably thermally hardenable. This preferably visible light- and 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. In this way a daylight stable printing plate may be obtained.

[0041] 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 or a benzophenone.

[0042] The ratio between the total amount of low molecular acid or benzophenone 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.

[0043] In the imaging element according to the present invention, the lithographic base may 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 may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in **GB-A- 1 084 070, DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760** and **US-P- 4 458 005**.

[0044] According to another mode 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.

[0045] 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.

[0046] 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.

[0047] A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert

particles of larger size than the colloidal silica may be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

[0048] 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.

[0049] 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**.

[0050] 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.

[0051] 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.

[0052] 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 may 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.

[0053] 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 those that are used for developing conventional positive working presensitised printing plates, preferably containing SiO_2 in the form of silicates and having 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 are cleaned-out whereby a positive working printing plate is obtained.

[0054] In the present invention, the composition of the developer used is also very important.

[0055] Therefore, to perform development processing stably for a long time period particularly important are qualities such as strength of alkali and the concentration 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.

[0056] 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.

[0057] 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.

[0058] In the present invention, particularly important is the molar ratio in the developer of $[SiO_2]$ / $[M_2O]$, which is generally 0.6 to 1.5, preferably 0.7 to 1.3. This is because if the molar ratio is less than 0.6, 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.

[0059] 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.

[0060] 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.

[0061] 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 (C_8 - C_{22}) 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.

[0062] In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0063] 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 $[Co(NH_3)_6]Cl_3$ 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**.

[0064] 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**.

[0065] 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.

[0066] 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.

[0067] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

Examples

Example 1

Preparation of the lithographic base

[0068] A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 to form a surface topography with an average center-line roughness Ra of 0.5 μm.

[0069] 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.

[0070] 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 subsequently with a solution containing aluminum trichloride, rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the heat-mode imaging element 1.

[0071] On the lithographic base was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14μm. The resulting layer contained 88% of ALNOVOL SPN452 ™ and 12% of 3,4,5-trimethoxybenzoic acid. Upon this layer was then coated with a wet coating thickness of 20μm, the IR-sensitive layer from a 0.885% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of 120°C.

The resulting IR-sensitive layer contained 115 mg/m^2 of carbon black, 11.5 mg/m^2 of nitrocellulose, 2.1 mg/m^2 of SCLSPERSE 5000 ™, (available from Zeneca Specialities, GB) 11.3 mg/m^2 of SOLSPERSE 28000 ™ and 14 mg/m^2 of FLUORAD FC 431 ™.

FLUORAD FC 431 ™ is a non-ionic perfluoroaliphatic polymeric ester, available from 3M, USA.

Preparation of the heat-mode imaging element 2.

[0072] Said element was prepared in an identical way as element 1 with the exception that no FLUORAD FC 431 ™ was used in the top layer

[0073] The two elements were imaged with a GERBER C42T ™ (available from Gerber) internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 4W.

After IR-imaging the materials were developed at 1m/min at 25°C in a TECHNIGRAPH NPX-32T ™ (available from Technigraph) processor using OZASOL EP 26 ™ (9 parts OZASOL EP 26 ™ and 1 part of water - OZASOL EP 26 ™ is commercially available from Agfa, Germany). In element 1 the IR-exposed areas dissolved very rapidly without any attack in the non-IR-exposed areas, resulting in a positive working plate. Said plate could be printed on a Heidelberg GTO 46 printing machine with a conventional ink from K+E and fountain solution from Rotamatic resulting in good prints, i.e. no scumming in the imaged areas and good ink-uptake in the non-IR-exposed areas. In element 2, the IR-exposed areas dissolved very rapidly but the non-IR-exposed areas were at the same time severely attacked and no good image formation on the printing plate resulted.

Example 2

Preparation of the heat-mode imaging element 3.

[0074] On the lithographic base of example 1 was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14μm. The resulting layer contained 88% of ALNOVOL SPN452 ™ and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was then coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 0.3% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of 120°C.

[0075] The resulting IR-sensitive layer contained 35 mg/m^2 IR-dye compound 1, 10 mg/m^2 dye BASONYL-BLAU 636 ™ (a triarylmethane dye commercially available from BASF), 2 mg/m^2 TEGOGLIDE 265 ™ (polyether siloxane copolymer) and 5 mg/m^2 TEGOGLIDE 410 ™ (polyether modified polysiloxane) (both silicon surfactants commercially available from Tego Chemie Service GmbH).

[0076] This material was imaged with a CREO TRENDSETTER 3244-T ™ external drum platesetter (available from Creo)at 2400 dpi with an energy-density of 186 mJ/cm^2 at 150 rpm.

[0077] After IR-imaging the material was developed at 1 m/min at 25°C in a TECHNIGRAPH NPX-32T ™ processor using OZASOL EP26 ™ developer (commercially available from Agfa).

[0078] The IR-exposed areas dissolved very rapidly without any attack in the non IR-exposed areas, resulting in a positive working printing plate.

[0079] The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E800) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non imaged areas.

Comparitive heat-mode imaging element 4:

[0080] - In this comparitive element 4 the surfactants TEGO GLIDE 265 ™ and TEGO GLIDE 410 ™ were left out of the IR-sensitive top layer of the heat-mode imaging element 3. This material was imaged with a CREO TRENDSETTER 3244-T ™ external drum platesetter at 2400 dpi with an energy-density of 186 mJ/cm^2 at 150 rpm.

[0081] After IR-imaging the material was developed at 1 m/min at 25°C in a TECHNIGRAPH NPX-32T ™ processor using OZASOL EP26 ™ developer (commercially available from Agfa).

[0082] The IR-exposed areas dissolved very rapidly with severe attack of the non IR-exposed areas, resulting in a useless printing plate.

[0083] Printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E800) and fountain solution (Rotamatic), the plate gave no good printing result i.e. no good ink-uptake in the non imaged areas.

[0084] Results: Density of the layer and Dmax / Dmin after imaging and processing were measured with MacBeth 918SB (cyan filter).

	Before processing	After processing	
Material	Dmax	Dmax	Dmin
example A	0.55	0.55	0.02
comparitive example	0.54	0.39	0.02

Claims

1. A heat mode imaging element for making a lithographic printing plate having on a lithographic base with a hydrophilic surface a first layer including a polymer that is soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer that is IR-sensitive and unpenetrable for an alkaline developer; characterized in that at least one of said first layer and said top layer comprises a surfactant.

2. A heat mode imaging element for making a lithographic printing plate according to claim 1 wherein said surfactant is a surfactant selected from the group consisting of perfluoroalkyl surfactants, and alkylphenyl surfactants.

3. A heat mode imaging element for making a lithographic printing plate according to claim 1 wherein said surfactant

is a polysiloxane surfactant.

4. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 3 wherein the surfactant is present in an amount ranging from 0.003 to 0.050 g/m^2.

5. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 4 wherein said polymer included in the first layer is a hydrophobic polymer.

6. A heat mode imaging element for making a lithographic printing plate according to claim 5 wherein said hydrophobic polymer is a novolac resin or a polymer comprising hydroxystyrene units.

7. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 6 wherein said first layer comprises a compound selected from the group consisting of low molecular acids and benzophenones.

8. A heat mode imaging element for making a lithographic printing plate according to any of claims 1 to 7 wherein the lithographic base is an electrochemically grained and anodised aluminum support.

9. A heat mode imaging element for making a lithographic printing plate according to claim 8 wherein the electrochemically grained and anodised aluminum support has been 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.

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

a) exposing imagewise a heat mode imaging element according to any of claims 1 to 9 to IR-radiation;
b) developing said imagewise exposed heat mode imaging element with an aqueous 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.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 0511

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 July 1999	Rasschaert, A

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