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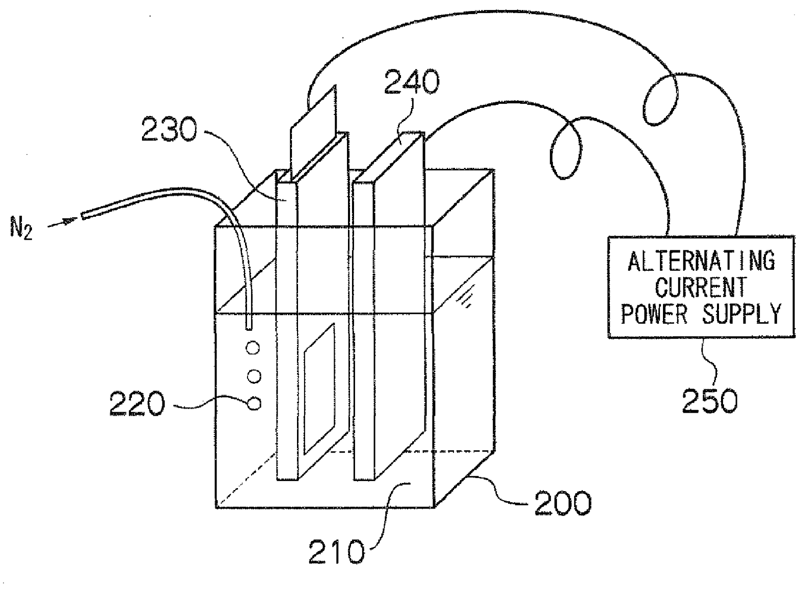
(54) Method for producing lithographic printing plate original plate and method for roughening surface of aluminium support body

(57) There is provided a method of producing a lithographic printing plate original plate and a method for roughening a surface of an aluminum support body, wherein pits having a smaller average pit diameter and being uniform in diameter can be dispersedly formed on the surface of the aluminum support body, with a high density.

In a method for producing a lithographic printing plate original plate, the method comprising an electrolytic surface-roughening treatment step for an aluminum support body (230), an electrolysis treatment is performed in an acidic solution (210) having a dissolved oxygen concentration of 6.0 mg/l or less in the electrolytic surface-roughening treatment step.

FIG. 2



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a method for producing a lithographic printing plate original plate and a method for roughening a surface of an aluminum support body, and particularly relates to a method for producing a lithographic printing plate original plate and a method for roughening a surface of an aluminum support body, wherein diameters of pits formed when the aluminum support body used for a lithographic printing plate is electrolytically surface-roughened can be made uniform.

Description of the Related Art

[0002] Conventionally, when a photosensitive composite for coloring, dyeing, coating, or lithographic printing is prepared on pure aluminum or aluminum alloy (hereinafter may be referred to as "aluminum") and aluminum on which an anodic oxide film is formed, roughening of the aluminum support body surface has been generally performed as a method for increasing adhesion to the aluminum support body.

[0003] The roughening of the aluminum support body surface is carried out by electrolyzing the aluminum support body and is designated as an electrolytic surface-roughening treatment.

[0004] The electrolytic surface-roughening treatment is performed by applying an alternating waveform current such as a sine wave current, a rectangular wave current, or a trapezoid wave current, or a direct current, to the aluminum support body in an acidic electrolyte.

[0005] The acidic electrolyte used for the electrolytic surface-roughening treatment is usually nitric acid, sulfuric acid, phosphoric acid, or a mixed solution obtained by mixing nitric acid, sulfuric acid, and phosphoric acid at a certain ratio.

[0006] In the electrolytic surface-roughening treatment by an alternating current, pits are formed by an anode reaction, however, an oxide film is also simultaneously formed, whereby surface resistance is increased and dispersibility of the pits is reduced. When dispersibility of pits is reduced, pits with uneven diameters are prone to be formed. Accordingly, a surface area of the aluminum support body does not become so large, whereby poor adhesion to an upper layer is caused.

[0007] In the electrolytic surface-roughening treatment by a direct current, an anodic oxide film is formed on the aluminum support body, however, concentration of oxygen which is dissolved in the acidic electrolyte (hereinafter, referred to as dissolved oxygen) is not constant, whereby unevenness in quality among products develops.

[0008] As a device for dispersing pits, for example, Japanese Patent No. 2614744 can be mentioned. In the Japanese Patent No. 2614744, preferable is a method for performing a surface-roughening treatment after preparing an organic film or an inorganic film each of which has electric resistance.

SUMMARY OF THE INVENTION

[0009] However, in the Japanese Patent No. 2614744, there are problems where it is difficult to control thickness of the organic film or the inorganic film, and an electrolyte is contaminated.

[0010] The present invention has been made in view of such problems and has an object to provide a method for increasing adhesion to an upper layer by controlling formation of an oxide film to disperse pits and to uniformize the pits when the aluminum support body is surface-roughened in the acidic solution by alternating current electrolysis treatment. The present invention also has an object to provide a method for generating an anode oxide film with prescribed thickness and characteristic to control qualitative variation among products when surface-roughening by the anode reaction of the direct current electrolysis treatment.

[0011] The above-mentioned problems can be solved by the following invention. That is, a method of producing a lithographic printing plate in the present invention is a method of producing a lithographic printing plate comprising an electrolytic surface-roughening treatment step of performing an electrolytic surface-roughening treatment of the aluminum support body, and is mainly characterized in that, in the electrolytic surface-roughening treatment step, an electrolysis treatment is performed in an acidic solution with a dissolved oxygen concentration of 6.0 mg/l or less.

[0012] Furtheremore, a surface-roughening method of a surface of the aluminum support body in the present invention is mainly characterized in that electrolysis treatment of the aluminum support body is performed in an acidic solution having a dissolved oxygen concentration of 6.0 mg/l or less.

[0013] Thus, formation of the oxide film in the anode reaction in the alternating current electrolysis treatment is kept under control, surface resistance is reduced, and a current is applied uniformly, whereby pits having a smaller average pit diameter and being uniform in diameter can be formed with high density. A pit evaluation was performed by analyzing

SEM photographs. Moreover, thickness and characteristics of the anodic oxide film formed by the anode reaction in the direct current electrolysis treatment are determined only by oxygen ions generated by water dissociation since an influence by dissolved oxygen becomes smaller, and therefore product quality can be made uniform.

[0014] In the present invention, the concentration of the dissolved oxygen in the acidic solution is 6 mg/l or less, and preferably 3 mg/l or less, and more preferably 1 mg/l or less. A dissolved oxygen analyzer (made by Central Kagaku Corp.) was used for concentration measurement.

[0015] A method for removing dissolved oxygen is any of film degassing, a nitrogen purge, and a pressure reduction. Any of these methods is a method for connecting with an exhaust pipe portion between an electrolytic bath and an electrolyte tank and thereby circulating a solution in which a concentration of dissolved oxygen becomes a certain degree or less.

[0016] The pressure reduction is a method for reducing a concentration of dissolved oxygen in an acid electrolytic solution by exposing the acid electrolytic solution to a pressure-reduced atmosphere.

[0017] The nitrogen purge is a method for substituting dissolved oxygen by passing nitrogen gas through an acid electrolytic solution to reduce a concentration of dissolved oxygen.

[0018] The film degassing is, for example, a method for removing oxygen by using a deoxidizing resin in which a weak-base anion exchange resin holds reducible copper, and a method by using a film degassing device equipped with a degassing film having a property of passing through a gas such as oxygen, but preventing liquid permeation.

[0019] According to the present invention, in the surface-roughening treatment by using electrolysis, pits having a smaller average pit diameter and being uniform in diameter can be formed with high density.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a sectional view showing an example of an electrolytic surface-roughening treatment apparatus equipped with a radial-type alternating current electrolytic bath in an embodiment of the present invention.

Fig. 2 is a diagram illustrating an example of an apparatus used for an electrolytic surface-roughening method according to the present invention.

Fig. 3 is a SEM photograph of a surface of the aluminum support body after the surface-roughening treatment.

Fig. 4 is another SEM photograph of a surface of the aluminum support body after the surface-roughening treatment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] Hereinafter, the preferred embodiments of the present invention are described.

[Electrolysis Treatment Method]

[0022] As an acidic solution used by the present invention, a nitric acid solution, a hydrochloric acid solution, a phosphoric acid solution, and a mixed solution of a nitric acid solution, a hydrochloric acid solution, and a phosphoric acid solution can be mentioned, however, a nitric acid solution is preferable. A concentration of the nitric acid solution is preferably 1 to 20 g/l, and more preferably 5 to 15 g/l. A solution temperature at the time of the electrolysis treatment is preferably 20 to 60 °C, and more preferably 30 to 50 °C. A current density in alternating current electrolysis is preferably 10 to 60 A/dm^2, and more preferably 25 to 55 A/dm^2. A total quantity of electricity is preferably 10 to 400 C/dm^2, and more preferably 60 to 300 C/dm^2. A distance between aluminum and a carbon electrode is preferably 5 to 50 mm, and more preferably 10 to 20 mm.

[Production of a support body for a lithographic printing plate and of a lithographic printing plate original plate]

[0023] Hereinafter, the present embodiment describes an example in which the present invention is applied to an alternating current roughening treatment performed by using a nitric acid solution, in a step of producing the aluminum support body for the lithographic printing plate.

[0024] Fig. 1 illustrates a schematic diagram of a sectional view showing an example of the electrolytic surface-roughening treatment apparatus which is preferably used for the present invention and equipped with the radial-type alternating current electrolytic bath.

[0025] As shown in Fig. 1, an electrolytic surface-roughening treatment apparatus 10 comprises an electrolytic bath main body 12 inside which an electrolytic bath 12A for storing an acidic electrolyte is provided; and a feeding roller 14 which is rotatably disposed around an axis extended horizontally inside the electrolytic bath 12A, and feeds an aluminum web W in a direction of an arrow a, that is, from right to left in Fig. 1, the aluminum web W being a continuous belt-like thin plate.

[0026] An interior wall surface of the electrolytic bath 12A is formed substantially cylindrically so as to surround the feeding roller 14, and on the interior wall surface of the electrolytic bath 12A, semi-cylindrical electrodes 16A and 16B are provided so as to sandwich the feeding roller 14. The electrodes 16A and 16B are divided into a plurality of small electrodes 18A and 18B along a direction of the circumference, respectively, and insulating layers 20A and 20B are equipped between the small electrodes 18A and 18B, respectively. The small electrodes 18A and 18B can be formed by using, for example, graphite, metal, etc., and the insulating layers 20A and 20B can be formed by using, for example, polyvinyl chloride resin, etc. Thickness of the insulating layers 20A and 20B is preferably 1 to 10 mm. In addition, in both of the electrodes 16A and 16B, the small electrodes 18A and 18B are connected to an AC power supply, respectively. Each of the small electrodes 18A and 18B and the insulating layers 20A and 20B as held by an insulating electrode holder 20C to form the electrodes 16A and 16B, respectively.

[0027] The AC power supply has a function which supplies an alternating waveform current to the electrodes 16A and 16B. As the AC power supply, there can be mentioned a sine wave generating circuit in which a sine wave is generated by a current and voltage regulation of a commercial alternating current, with using an induction regulator and a transformer; a thyristor circuit in which a trapezoid wave current or a rectangular wave current is generated from a direct current obtained by rectifying a commercial alternating current; etc.

[0028] In the upper part of the electrolytic bath 12A, there is formed an opening 12B through which the aluminum web W, being an example of a metal plate in the embodiment and being a continuous beltlike aluminum plate, is drawn in and out at the time of the alternating-current electrolysis surface-roughening treatment. In the vicinity of the downstream end of the electrode 16B in the opening portion 12B, an acidic electrolyte replenishment path 22 which replenishes the electrolytic bath 12A with an acidic electrolyte is provided. As such acidic electrolyte, a nitric acid solution, a hydrochloric acid solution, etc. can be used.

[0029] In the vicinity of the opening portion 12B in the upper part of the electrolytic bath 12A, disposed are a group of upstream guide rollers 24A which guide the aluminum web W to the interior of electrolytic bath 12A; and downstream guide rollers 24B which guide the aluminum web W, already given electrolytic surface-roughening treatment inside the electrolytic bath 12A, to the exterior of the electrolytic bath 12A.

[0030] An overflow bath 12C is provided at an upstream side of the electrolytic bath 12A in the electrolytic bath main body 12. The overflow bath 12C has a function to temporarily store an acidic electrolyte which overflows the electrolytic bath 12A to maintain the height of a liquid level of the electrolytic bath 12A.

[0031] In the electrolyte in the vicinity of the entrance portion which guides the aluminum web W to the interior of electrolytic bath 12A, a direct-current portion 26, which impresses negative direct-current voltage to the aluminum web W, is provided at a position of 5 to 15 mm from a surface of the aluminum web W. The direct-current portion 26 has a function to impress negative direct-current voltage to the aluminum web W to pass a direct current through the aluminum web W, in the entrance inside the electrolytic bath 12A all the time.

[0032] An auxiliary electrolytic bath 28 is provided at a downstream side of the electrolytic bath 12A in the electrolytic bath main body 12. The auxiliary electrolytic bath 28 is shallower than the electrolytic bath 12A, and a bottom 28A is formed flat. In addition, a plurality of cylindrical auxiliary electrodes 29 is provided on the bottom 28A.

[0033] The auxiliary electrode 29 is preferably formed from high corrosion resistance metal such as platinum, ferrite, etc. and may be formed in a plate form.

[0034] The auxiliary electrodes 29 are connected to a side to which the electrode 16A in the AC power supply is connected, in parallel to the electrode 16A, and a thyristor Th1 is connected in-between so that a current could flow in a direction from a side connected to the electrode 16A in the AC power supply toward the auxiliary electrodes 29 at the time of ignition.

[0035] In addition, the auxiliary electrode 29 is also connected, via a thyristor Th2, to a side to which the electrode 16B in the AC power supply is connected. The thyristor Th2 is connected so that a current could flow in a direction from a side connected to the electrode 16B in the AC power supply toward the auxiliary electrodes 29 at the time of ignition.

[0036] When either of the thyristors Th1 and Th2 is ignited, an anode current flows into the auxiliary electrodes 29. Therefore, by carrying out a phase control of the thyristors Th1 and Th2, a current value of the anode current which flows into the auxiliary electrode 29 can be controlled, and also a ratio Qc/Qa, where Qc is a quantity of electricity which flows when the aluminum web W is a cathode and Qa is a quantity of electricity which flows when the aluminum web W is an anode, can be controlled.

[0037] Moreover, the auxiliary electrodes 29 and the direct-current part 26 are connected through a direct current power supply.

[0038] The frequency of the alternating current is not particularly limited, but preferably 40 to 120 Hz, more preferably 40 to 80 Hz, and still more preferably 50 to 60 Hz.

[0039] For the aluminum web W, the ratio Qc/Qa, where Qc is a quantity of electricity which flows at the time of a cathode reaction and Qa is a quantity of electricity which flows at the time of an anode reaction, is preferably 0.9 to 1, and more preferably 0.95 to 0.99. Thus, uniform honeycomb pits can be formed on the surface of the aluminum web W.

[0040] The duty of the alternating current is not particularly limited, but, from viewpoints of uniformly providing the surface-roughening treatment to the surface of the aluminum web W and of manufacturing an power supply unit, preferably 0.33 to 0.66, more preferably 0.4 to 0.6, and most preferably 0.5. In the present embodiment, "duty" means ta/T, where T is an alternating current period and ta is a time of an anode reaction of an aluminum alloy plate (anode reaction time).

[0041] TP, which is a time until a current value of an alternating current reaches a positive or negative peak from zero, is preferably 0.5 to 6 msec, and more preferably 0.6 to 5 msec, in the case of a trapezoid wave current. Thus, more uniform and crater-like depressed portions can be formed on the surface of the aluminum web W.

[0042] An quantity of electricity which flows from the starting time until the finishing time of the electrolytic surface-roughening treatment is preferably 10 to 1000 C/dm^2, more preferably 10 to 800 C/dm^2, and still more preferably 40 to 500 C/dm^2, in total when the aluminum web W is an anode.

[0043] Each of I ap, a current at the time of a peak at an anode cycle side of an alternating current, and I cp, a current at the time of a peak at a cathode cycle side of an alternating current, is preferably 10 to 100 A/dm^2, more preferably 20 to 80 A/dm^2, and still more preferably 30 to 60 A/dm^2. Moreover, I cp/I ap is preferably 0.9 to 1.5, and more preferably 0.9 to 1.0.

[0044] In the electrolytic surface-roughening treatment, it is preferable that, in one or two or more electrolytic baths, one or more idle period in which an alternating current does not flow into the aluminum web W is provided, and a length of the idle period is 0.001 to 0.6 second, whereby honeycomb pits are uniformly formed on the whole surface of the aluminum web W.

[0045] As an example where the present invention is applied, a method for producing the lithographic printing plate original plate is described. Here, the lithographic printing plate original plate is a plate before producing a lithographic printing plate, and the lithographic printing plate is produced by image-exposing and developing the plate.

<Aluminum Web (Rolled Aluminum)>

[0046] An aluminum plate used as the aluminum web W in the present embodiment is a metal including aluminum, which is stable in terms of size, as a major constituent. As mentioned above, the aluminum alloy plate is also included as the aluminum plate, hereinafter, these plates are collectively called an aluminum plate.

[0047] As the aluminum plate, a plastic film or paper on which an aluminum alloy is laminated or vapor-deposited can also be used. Furthermore a complex sheet obtained by bonding an aluminum sheet onto a polyethylene terephthalate film can also be used. Moreover, the aluminum plate may also include elements such as Bi and Ni, and inevitable impurities.

[0048] As the aluminum plates, aluminum alloy plates which are conventionally known and used, such as JIS A1050, JIS A1100, JIS A3003, JIS A3004, JIS A3005, and an international registration alloy 3103A, can be suitably used.

[0049] A method for producing the aluminum plate may be either of a continuous casting method and a DC casting method. An aluminum plate produced by omitting intermediate annealing in the DC casting method and omitting a soaking treatment can also be used. An aluminum plate having projections and depressions given by pack-rolling, transferring, etc. can also be used in finish rolling. Moreover, the aluminum plate may be an aluminum web which is a continuous belt-like sheet material or plate material, or may be a leaf-like sheet which is cut into a size corresponding to the lithographic printing plate original plate to be shipped as a product.

[0050] Thickness of the aluminum plate is usually approximately 0.05 mm to 1 mm, and preferably 0.1 mm to 0.5 mm. The thickness can be suitably changed according to a size of a printing machine, a size of a printing plate, and a request by a user.

[0051] In the method for producing the lithographic printing plate original plate in the present embodiment, the lithographic printing plate original plate is obtained by performing various surface treatments including the electrolytic surface-roughening treatment in an acidic solution on the above-mentioned aluminum plate. These surface treatments may further include various kinds of treatments.

[0052] An alkali etching treatment or a desmut treatment is preferably performed before the electrolytic surface-roughening treatment, and it is also preferable that the alkali etching treatment and the desmut treatment are performed in this order. In addition, an alkali etching treatment or a desmut treatment is preferably performed after the electrolytic surface-roughening treatment, and it is also preferable that the alkali etching treatment and the desmut treatment are performed in this order. The alkali etching treatment after the electrolytic surface-roughening treatment may be omitted. In the present invention, mechanical surface-roughening treatment is also preferably performed before the alkali etching treatment and the desmut treatment. The electrolytic surface roughening treatment may be performed twice or more. Subsequently, an anodizing treatment, a pore-sealing treatment, a hydrophilization treatment, etc. are also preferably performed.

[0053] Hereafter, each of the mechanical surface-roughening treatment and a first alkali etching treatment, a first desmut treatment, the electrolytic surface-roughening treatment, a second alkali etching treatment, a second desmut treatment, the anodizing treatment, the pore-sealing treatment, and the hydrophilization treatment is described in detail.

It is note that, in the present embodiment, a treatment performed before the electrolytic surface-roughening treatment may be sometimes called with giving an ordinal number "first", while a treatment performed after the electrolytic surface-roughening treatment maybe sometimes called with giving an ordinal number "second".

<Mechanical surface-roughening treatment>

[0054] The mechanical surface-roughening treatment is preferably performed before the electrolytic surface-roughening treatment. The mechanical surface-roughening treatment is generally performed by brushing one side or both sides of the surface of the aluminum web by using a roller-shaped brush with spraying a slurry solution containing an abrasive on the roller-shaped brush which is rotating, the roller-shaped brush having a cylindrical body on a surface of which a large amount of brush hair, such as synthetic resin hair made from synthetic resins such as nylon (registered trademark), propylene, and vinyl chloride resin, is implanted. Instead of the roller-shaped brush and the slurry solution, a polishing roller which is a roller having a polishing layer on the surface can also be used. A length of the brush hair of the roller-shaped brush may be suitably determined according to an outer diameter and a body diameter of the roller-shaped brush, but is generally 10 to 100 mm.

[0055] As the abrasive, a known one can be used. For example, an abrasive, such as pumice stone, silica sand, aluminum hydroxide, alumina powder, volcanic ash, carborundum, and emery, or a mixture containing those abrasives can be used. Among these, pumice stone and silica sand are preferable, and particularly silica sand is more preferable from a viewpoint where silica sand is harder and more durable compared with pumice stone, thereby is excellent in surface-roughening efficiency. An average particle diameter of the abrasive is preferably 3 to 50 μm, and more preferably 6 to 45 μm, since surface-roughening efficiency is excellent and a graining pitch can be narrowed. When pumice stone is used as the abrasive, the average particle diameter is in particular preferably 40 to 45 μm, and when silica sand is used as the abrasive, the average particle diameter is in particular preferably 20 to 25 μm. The abrasive is, for example, made into a polishing slurry solution by suspending the abrasive in water and then used. Besides the abrasive, a thickener, a dispersing agent (for example, a surface active agent), an antiseptic agent, etc. may be contained in the polishing slurry solution. The average particle diameter means a particle diameter having 50% of a cumulative percentage in cumulative distribution of a percentage of the abrasive particles having each particle diameter in proportion to a volume of all the abrasives contained in the polishing slurry solution.

[0056] Moreover, in the mechanical surface-roughening treatment, a degreasing treatment for removing rolling oil on the surface of the aluminum web, for example, a degreasing treatment by using a surface active agent, an organic solvent, an alkaline solution, etc. may be first performed by request before performing brush-polishing.

<First Alkali Etching Treatment>

[0057] In a first alkali etching treatment, etching is performed by contacting the aluminum web with an alkali solution. When the mechanical surface-roughening treatment is not performed yet, the first alkali etching treatment is performed for a purpose of removing a rolling oil, contamination, and a natural oxidation film on the surface of the aluminum web (rolled aluminum), while when the mechanical surface-roughening treatment is already performed, the first alkali etching treatment is performed for a purpose of obtaining a smooth winding surface by dissolving edge portions with projections and depressions generated by the mechanical surface-roughening treatment. As the method for contacting the aluminum web with the alkali solution, for example, a method for making the aluminum web pass through a bath filled with an alkali solution, a method for soaking the aluminum web in a bath filled with an alkali solution, a method for spraying an alkali solution on the surface of the aluminum web, etc. can be mentioned.

[0058] An etching amount is preferably 1 to 15 g/m^2 for a surface to which the electrolytic surface-roughening treatment is given at a following step, and preferably 0.1 to 5 g/m^2 (approximately 10 to 40% of a surface to which the electrolytic surface-roughening treatment is given) for the surface to which the electrolytic surface-roughening treatment is not given.

[0059] As alkali used for the alkali solution, caustic alkali and alkali metal salt can be mentioned, for example. Specifically, as caustic alkali, caustic soda and caustic potash can be mentioned, for example. As alkali metal salt, for example, alkali metal silicates, such as sodium metasilicate, sodium silicate, potassium metasilicate, and potassium silicate; alkali metal carbonate, such as sodium carbonate and potassium carbonate; alkali metal aluminate, such as sodium aluminate and potassium aluminate; alkali metal aldonic acid salt, such as sodium gluconate and potassium gluconate; and alkali metal hydrogen phosphate, such as secondary sodium phosphate, secondary potassium phosphate, tertiary sodium phosphate, and tertiary potassium phosphate can be mentioned. Particularly, a caustic alkali solution and a solution containing both caustic alkali and alkali metal aluminate are preferable since these solutions exhibit a high etching speed and are inexpensive. In particular, a caustic sodium solution is more preferable.

[0060] A concentration of the alkali solution can be determined according to an etching amount, but is preferably 1 to 50% by mass, and more preferably 10 to 35% by mass. If aluminum ions are dissolved into the alkali solution, a concentration of the aluminum ions is preferably 0.01 to 10% by mass, and more preferably 3 to 8% by mass. A temperature of the alkali solution is preferably 20 to 90 °C. A treatment time is preferably 1 to 120 seconds. An amount of the etching treatment is preferably 1 to 15 g/m^2 dissolution, and more preferably 3 to 12 g/m^2 dissolution. The first alkali etching treatment can be performed by using an etching bath usually used for the etching treatment for the aluminum web. As the etching bath, either of a batch-type or a continuous-etching bath can be used. Moreover, when the first alkali etching treatment is performed by spraying the alkali solution on a surface of the aluminum web, a spray apparatus can be used.

<First Desmut Treatment>

[0061] A first desmut treatment is performed by, for example, contacting the aluminum web with an acidic solution of hydrochloric acid, nitric acid, sulfuric acid, etc. with a concentration of 0.5 to 30% by mass (containing aluminum ions of 0.01 to 5% by mass). As the method for contacting the aluminum web with the acidic solution, for example, a method for making the aluminum web pass through a bath filled with an acidic solution, a method for soaking the aluminum web in a bath filled with an acidic solution, a method for spraying an acidic solution on a surface of the aluminum web, etc. can be mentioned. In the first desmut treatment, as the acidic solution, preferably used are a waste liquid of an aqueous solution containing mainly nitric acid or an aqueous solution containing mainly hydrochloric acid, the waste liquid being discharged in the electrolytic surface-roughening treatment mentioned later, or a waste liquid of an aqueous solution containing mainly sulfuric acid, the waste liquid being discharged in the anodizing treatment mentioned later. A solution temperature in the first desmut treatment is preferably 25 to 90 °C. Moreover, a treatment time of the first desmut treatment is preferably 1 to 180 seconds.

<Electrolytic Surface-roughening Treatment>

[0062] An acidic solution used in the electrolytic surface-roughening treatment is not particularly limited, but an aqueous solution containing mainly nitric acid and an aqueous solution containing mainly hydrochloric acid are preferably used. The aqueous solution containing mainly nitric acid has a nitric acid concentration of preferably 3 to 20 g/L, and more preferably 5 to 15 g/L, and has an aluminum ion concentration of preferably 3 to 15g/L, and more preferably 3 to 7 g/L. The aluminum ion concentration in the aqueous solution containing mainly nitric acid can be adjusted by adding an aluminum nitrate to a nitric acid solution having the above-mentioned nitric acid concentration. The aqueous solution containing mainly hydrochloric acid has a hydrochloric acid concentration of preferably 3 to 15 g/L, and more preferably 5 to 10g/L, and has a aluminum ion concentration of preferably 3 to 15 g/L, and more preferably 3 to 7 g/L. The aluminum ion concentration in the aqueous solution containing mainly hydrochloric acid can be adjusted by adding aluminum chloride to a hydrochloric acid aqueous solution having the above-mentioned hydrochloric acid concentration.

<Second Alkali Etching Treatment>

[0063] In a second alkali etching treatment, etching is performed by contacting the aluminum web with an alkali solution. As a kind of alkali, a method for contacting the aluminum web with an alkali solution, and an apparatus used for the method, the same ones as used in the first alkali etching treatment can be mentioned. An etching amount is preferably 0.001 to 5 g/m^2, more preferably 0.01 to 3 g/m^2, and still more preferably 0.05 to 2 g/m^2, for a surface to which the electrolytic surface-roughening treatment is given.

[0064] As alkali used for the alkali solution, the same ones as used in the first alkali etching treatment can be mentioned. A concentration of the alkali solution can be determined according to the etching amount, but is preferably 0.01 to 80% by mass, A temperature of the alkali solution is preferably 20 to 90 °C. A treatment time is preferably 1 to 60 seconds. If an acidic solution which contains 100 g/L or more of sulfuric acid and whose temperature is 60 °C or more is used in the second desmut treatment mentioned later, the second alkali etching treatment may be omitted.

<Second desmut treatment>

[0065] The second desmut treatment is performed by, for example, contacting the aluminum web with an acidic solution of phosphoric acid, hydrochloric acid, nitric acid, sulfuric acid, etc. having a concentration of 0.5 to 30% by mass (containing aluminum ions of 0.01 to 5% by mass). As a method for contacting the aluminum web with the acidic solution, the same one as used in the first desmut treatment can be mentioned. In the second desmut treatment, as the acidic solution, a waste liquid of an sulfuric acid solution which is discharged in the anodizing treatment mentioned later is preferably used. Moreover, instead of the waste liquid, there may be used a sulfuric acid solution having a sulfuric acid concentration of 100 to 600 g/L, an aluminum ion concentration of 1 to 10 g/L, and a solution temperature of 60 to 90 °C. A solution temperature in the second desmut treatment is preferably 25 to 90 °C. A treatment time of the second desmut treatment is preferably 1 to 180 seconds. Aluminum and aluminum alloy components may be dissolved in the acidic solution used for the second desmut treatment.

<Anodizing Treatment>

[0066] It is preferable that the anodizing treatment is additionally performed to the aluminum web treated as mentioned above. The anodizing treatment can be performed by conventional methods in this field. Specifically, a direct current, a pulsating current, or an alternating current is made flow into the aluminum web in an electrolyte of an aqueous solution or a nonaqueous solution, the aqueous solution or the nonaqueous solution being obtained by using, alone or in combination of two or more kinds, sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid, amidosulfonic acid, etc., whereby an anodic oxide film can be formed on the surface of the aluminum web.

[0067] In particular, a sulfuric acid solution is preferably used as the electrolyte. In the electrolyte, a sulfuric acid concentration is preferably 10 to 300 g/L (1 to 30% by mass), and an aluminum ion concentration is preferably 1 to 25 g/L (0.1 to 2.5% by mass), and more preferably 2 to 10 g/L (0.2 to 1 % by mass). Such electrolyte can be prepared by, for example, adding aluminum to dilute sulfuric acid having a sulfuric acid concentration of 50 to 200 g/L.

[0068] When the anodizing treatment is performed in the electrolyte containing sulfuric acid, a direct current may be applied to the aluminum web and an alternating current may be applied thereto. When a direct current is applied to the aluminum web, a current density is preferably 1 to 60 A/dm^2, and more preferably 5 to 40 A/dm^2. When the anodizing treatment is performed continuously, it is preferable that a current is made to flow with a low current density of 5 to 10 A/dm^2 at the beginning of the anodizing treatment, and then, as the anodizing treatment proceeds, the current density is increased to be 30 to 50 A/dm^2 or more, so that what is called "burning" due to concentrating a current on a part of the aluminum web would not be caused. When the anodizing treatment is performed continuously, it is preferable that the treatment is performed by an electrolyte power supply method for supplying electric power to the aluminum web via the electrolyte.

[0069] As an electrode which supplies electric power to the aluminum web, an electrode formed of lead, iridium oxide, platinum, ferrite, etc. can be used. Particularly, an electrode which is formed of mainly iridium oxide and an electrode in which a surface of a base material is covered with iridium oxide are preferable. As such base material, it is preferable to use what is called valve metal, such as titanium, tantalum, niobium, and zirconium, and particularly titanium and niobium are more preferable among the valve metals. Since electric resistance of the valve metal is comparatively higher, the base material may be formed by cladding the valve metal on the surface of a core material made from copper. When the valve metal is clad on the surface of the core material made from copper, it is hard to produce a base material having a complicated shape, therefore the valve metal is clad to a core material configured by dividing the base material by parts, and then the base material may be assembled by combining each of the parts.

[0070] A condition of the anodizing treatment changes variously according to an electrolyte to be used, thereby cannot be determined as a whole, but generally an electrolyte concentration of 1 to 80% by mass, a solution temperature of 5 to 70 °C, a current density of 1 to 60 A/dm^2, a voltage of 1 to 100V, and an electrolysis time of 10 to 300 seconds are suitable. From a viewpoint of rigidity of the lithographic printing plate, the anodizing treatment is preferably performed so that an amount of the anodic oxide film would become 1 to 5 g/m^2. Moreover, the anodizing treatment is preferably performed so that difference of an anodic oxide film amount between in a central part of the aluminum web and in the vicinity of the edge of the aluminum web would be 1 g/m^2 or less.

<Pore-sealing Treatment>

[0071] The pore-sealing treatment is preferably performed, wherein small pores (micropores) formed by the anodizing treatment are sealed by contacting an aluminum alloy plate in which an anodic oxide film is formed, with boiling water, hot water, or steam.

<Hydrophilization Treatment>

[0072] After the anodizing treatment or the pore-sealing treatment, the hydrophilization treatment is preferably performed by a method for soaking in an aqueous solution of alkali metal silicate, such as sodium silicate or potassium silicate, a method for forming a hydrophilic undercoat layer by applying a hydrophilic vinyl polymer or a hydrophilic compound, etc. As the hydrophilic vinyl polymer used for the method, there can be mentioned, for example, a copolymer of a vinyl polymer compound containing sulfonic acid group, such as polyvinyl sulfonic acid and p-styrene sulfonic acid having a sulfonic acid group, and an ordinal vinyl polymer compound, such as (meta)acrylic acid alkyl ester. Moreover, as the hydrophilic compound used for the method, there can be mentioned, for example, a compound having at least one selected from a group including a $-NH_2$ group, a -COOH group, and a sulfo group.

[Formation of Intermediate Layer and Photosensitive Layer]

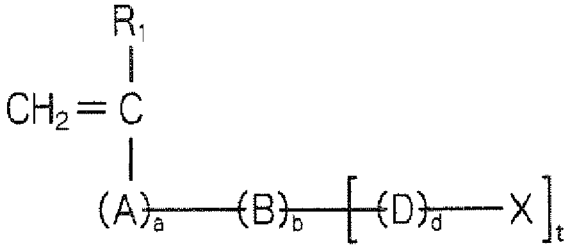
<Intermediate Layer>

[0073] A photosensitive layer may be provided directly on the support for lithographic printing plates to which the hydrophilization treatment is given or a support for lithographic printing plates to which the acidic solution treatment is additionally given after the hydrophilization treatment, and also, as necessary, an intermediate layer may be provided on each of the above-mentioned supports and then a photosensitive layer may be provided on the intermediate layer.

(Intermediate Layer of Macromolecular Compound having Acid Radical and Onium Group)

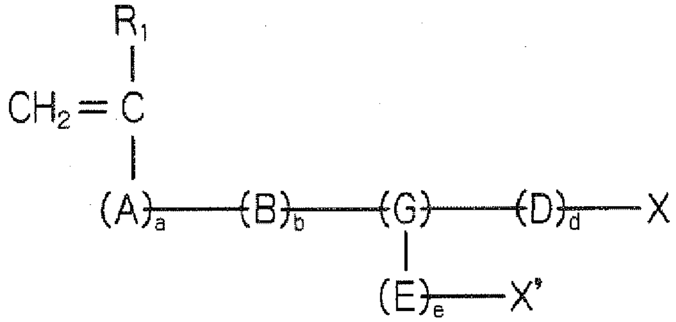
[0074] As a macromolecular compound used for the intermediate layer formation, more preferably used is a macromolecular compound which has an acid radical or has a component with an acid radical and a component with an onium group. The acid radical of the component of the macromolecular compound is preferably an acid radical having an acid dissociation index (pKa) of 7 or less, more preferably -COOH, $-SO_3H$, $-OSO_3H$, and $-PO_3H_2$, $-OPO_3H_2$, $-CONHSO_2$, and $-SO_2NHSO_2-$, and still more preferably -COOH. A component having a suitable acid radical is a polymerizable compound expressed by general formulas (1) and (2) below.

[Chemical Formula 1]



$$CH_2=C(R_1)-(A)_a-(B)_b-[(D)_d-X]_t$$

(1)



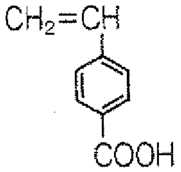
$$CH_2=C(R_1)-(A)_a-(B)_b-G\big((E)_e-X'\big)-(D)_d-X$$

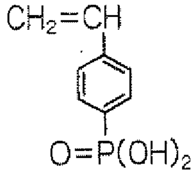
(2)

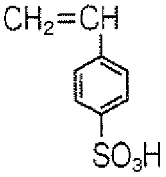
[0075] In the formulas, A represents a divalent linking group. B represents an aromatic group or a substituted aromatic group. Each of D and E independently represents a divalent linking group. G represents a trivalent linking group. Each of X and X' independently represents an acid radical of 7 or less pKa or its alkali metal salt, or an ammonium salt. R1 represents a hydrogen atom, an alkyl group, or a halogen atom. Each of a, b, d, and e independently represents 0 or 1. Moreover, t represents an integer of 1 to 3. Among the components having the acid radical, it is more preferable that A represents -COO- or CONH-, B represents a phenylene group or a substituted phenylene group, and its substituent group is a hydroxyl group, a halogen atom, or an alkyl group. Each of D and E independently represents an alkylene group, or a divalent linking group expressed by a molecular formula of $C_nH_{2n}O$, $C_nH_{2n}S$, or $C_nH_{2n+1}N$. G represents a trivalent linking group expressed by a molecular formula CnH_{2N-1}, CnH_{2n-10}, $CnH_{2n-1}S$, or $C_nH_{2n}N$. Here, n represents an integer of 1 to 12. Each of X and X' independently represents carboxylic acid, sulfonic acid, phosphonic acid, sulfuric acid monoester, or phosphoric acid monoester. R1 represents a hydrogen atom or an alkyl group. Each of a, b, d, and e independently represents 0 or 1, but a and b are not 0 simultaneously. Among the components having the acid radicals, a compound expressed by a general formula (1) is still more preferable, where B represents a phenylene group or a substituted phenylene group, and its substituent is a hydroxyl group or an alkyl group having a carbon number of 1 to 3. Each of D and E independently represents an alkylene group having a carbon number of 1 to 2 or an alkylene group having a carbon number of I to 2 and linked with an oxygen atom. R1 represents a hydrogen atom or a methyl group. X represents a carboxylic acid group. Moreover, a is 0, and b is 1.

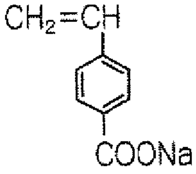
[0076] Examples of the components having the acid radicals are shown below, but the component is not limited to these examples. Acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, itaconic acid, maleic acid, maleic anhydride, etc. can be mentioned, and furthermore the followings can be mentioned.

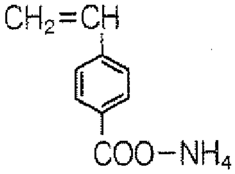
[Chemical formula 2]

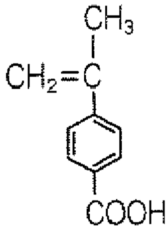


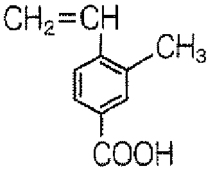


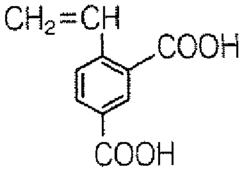




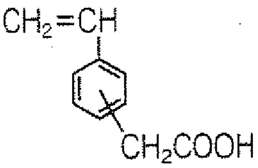


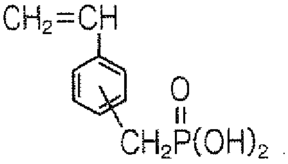


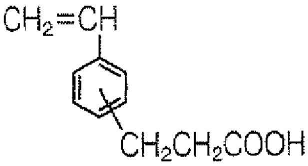


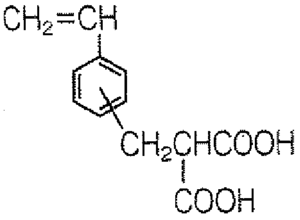


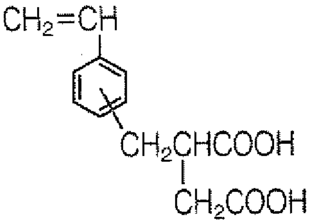
[Chemical formula 3]

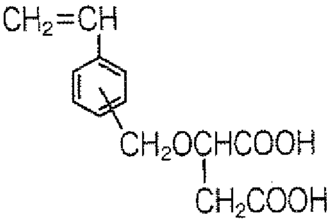


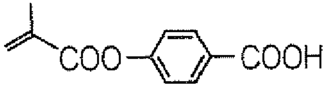


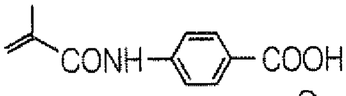


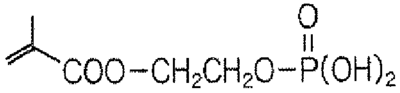


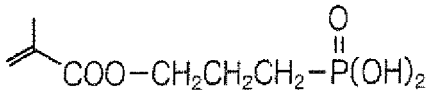




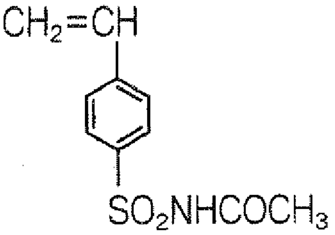


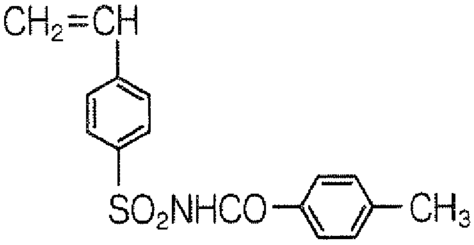


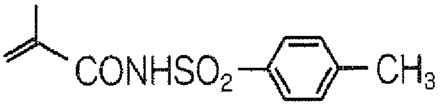


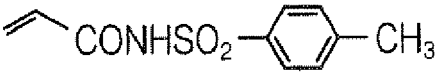


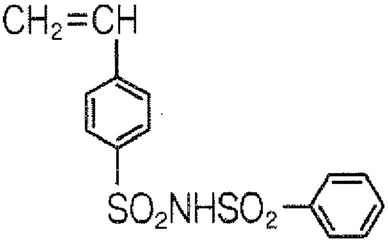
[Chemical formula 4]

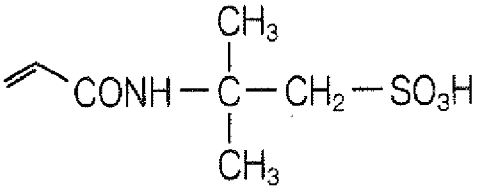


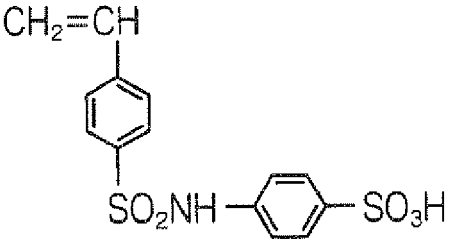










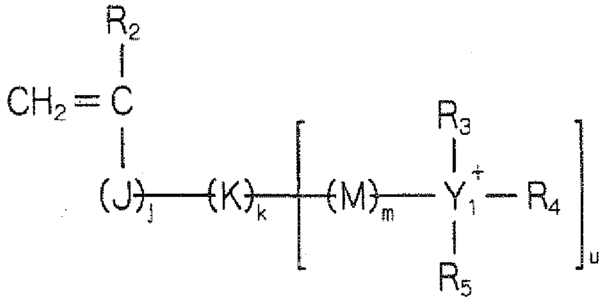


[0077] One kind or two or more kinds of the above-mentioned components having the acid radicals may be used alone or in combination.

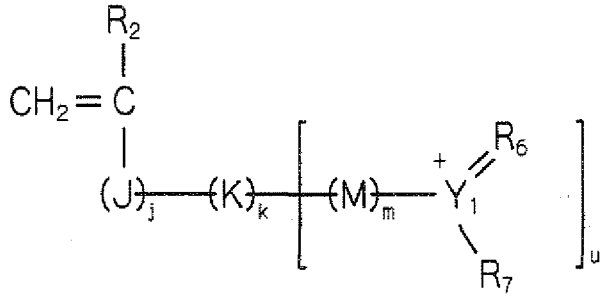
(Intermediate Layer of Macromolecular Compound having Onium group)

[0078] As an onium group of a component of a macromolecular compound used for forming the intermediate layer, preferable is an onium group including an atom of the fifth or sixth group of the periodic system, more preferable is an onium group including a nitrogen atom, a phosphorus atom, or a sulfur atom, and still more preferable is an onium group including a nitrogen atom. Moreover, as the macromolecular compound, preferable is a vinyl polymer having a backbone structure such as acrylate resin, methacrylic resin, and polystyrene, urethane resin, polyester, or a polymer being polyamide. In particular, more preferable is the vinyl polymer having a backbone structure such as acrylate resin, methacrylic resin, or polystyrene. As the macromolecular compound, still more preferable is a polymer being a polymerizable compound in which a component having an onium group is expressed by a general formula (3), a general formula (4), or a general formula (5), shown below.

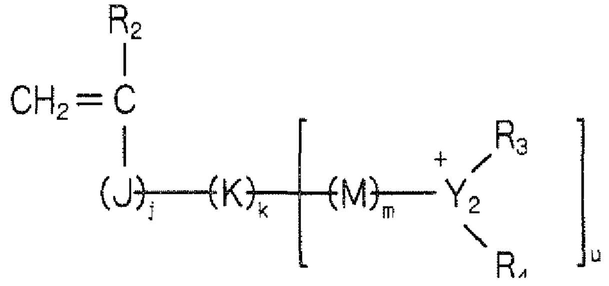
[Chemical formula 5]



$$CH_2{=}C(R_2){-}(J)_j{-}(K)_k{-}\left[(M)_m{-}\overset{R_3}{\underset{R_5}{Y_1^{+}}}{-}R_4\right]_u \quad uZ^- \qquad (3)$$



$$CH_2{=}C(R_2){-}(J)_j{-}(K)_k{-}\left[(M)_m{-}Y_1^{+}({=}R_6)(R_7)\right]_u \quad uZ^- \qquad (4)$$



$$CH_2{=}C(R_2){-}(J)_j{-}(K)_k{-}\left[(M)_m{-}Y_2^{+}(R_3)(R_4)\right]_u \quad uZ^- \qquad (5)$$

[0079] In the formulas, J represents a divalent linking group. K represents an aromatic group or a substituted aromatic group. M independently represents a divalent linking group. Y1 represents an atom of the fifth group of the periodic system, and Y2 represents an atom of the sixth group of the periodic system. Z- represents a counter anion. R2 represents a hydrogen atom, an alkyl group, or a halogen atom. Each of R3, R4, R5, and R7 independently represents a hydrogen atom, or, as necessary, an alkyl group, an aromatic group, and an aralkyl group to each of which a substituent may be linked, and R6 represents an alkylidyne group or a substituted alkylidyne group. R3 and R4, or R6 and R7 may be bound each other to form a ring. Each of j, k, and m independently represents 0 or 1. And, u represents an integer of 1 to 3.

Among the components having an onium group, it is more preferable that J represents -COO- or CONH-, K represents a phenylene group or a substituted phenylene group, and its substituent is a hydroxyl group, a halogen atom, or an alkyl group. M represents an alkylene group, or a divalent linking group expressed by a molecular formula of $C_nH_{2n}O$, $C_nH_{2n}S$, or $C_nH_{2n+1}N$. Here, n represents an integer of 1 to 12. Y1 represents a nitrogen atom or a phosphorus atom, and Y2 represents a sulfur atom. Z^- represents a halogen ion, PF_6^-, BF_4^-, or $R_8SO_3^-$. R2 represents a hydrogen atom or an alkyl group. Each of R3, R4, R5, and R7 independently represents a hydrogen atom, or, as necessary, an alkyl group, an aromatic group, or an aralkyl group each of which having a carbon number of 1 to 10 and to which a substituent may be linked, and R6 represents an alkylidyne group or a substituted alkylidyne group each of which having a carbon number of 1 to 10. R3 and R4, or R6 and R7 may be bound each other to form a ring. Each of j, k, and m independently represents 0 or 1, but j and k are not 0 simultaneously. Among the components having the onium group, it is still more preferable that K represents a phenylene group or a substituted phenylene group, and its substituent is a hydroxyl group or an alkyl group having a carbon number of 1 to 3. M represents an alkylene group having a carbon number of 1 to 2, or an alkylene group having a carbon number of 1 to 2 and linked to an oxygen atom. Z^- represents a chlorine ion or $R_8SO_3^-$. R2 represents a hydrogen atom or a methyl group. Moreover, j is 0, and k is 1.

<Photosensitive layer>

[0080] A lithographic printing plate original plate can be obtained by providing a photosensitive layer to a lithographic printing plate support before forming of the intermediate layer, or to a lithographic printing plate support in which the intermediate layer is formed.

[0081] The photosensitive layer is not particularly limited, but, for example, there can be mentioned a visible light exposure type platemaking layer which is exposed by ordinary visible light, and a laser exposure type platemaking layer which is exposed by laser light such as infrared laser light. Hereinafter, the visible light exposure type platemaking layer and the laser exposure type platemaking layer will be described.

(1) Visible Light Exposure Type Platemaking Layer

[0082] The visible light exposure type platemaking layer can be formed with a photopolymer, and as needed, a composite containing a colorant, etc. As the photopolymer, there can be mentioned a positive type photopolymer which dissolves in a developing solution when exposed to light, and a negative type photopolymer which does not dissolve in a developing solution when exposed to light. As the positive type photopolymer, there can be mentioned, for example, a combination of a diazide compound, such as a quinone diazide compound and a naphthoquinone diazide compound, and a phenol resin, such as a phenol novolak resin and a cresol novolak resin. As the negative type photopolymer, there can be mentioned, for example, a combination of: a diazo compound, such as a diazo resin (for example, a condensate of aromatic diazonium salt and aldehyde such as formaldehyde), an inorganic acid salt of the diazo resin, and an organic acid salt of the diazo resin; and a binder, such as a (meta)acrylate resin, a polyamide resin, and a polyurethane resin, and a combination of: a vinyl polymer, such as a (meta)acrylate resin and a polystyrene resin; a vinyl polymer compound, such as (meta)acrylic ester and styrene; and a photopolymerization initiator, such as a benzoin derivative, a benzophenone derivative, and a thioxanthone derivative.

[0083] As the colorant, besides a ordinal coloring matter, there can be used an exposure color-development coloring matter which is color-developed by exposure, and an exposure color-disappearing coloring matter which becomes almost or completely colorless by exposure. As the exposure color-development coloring matter, a leuco coloring matter can be mentioned, for example. As the exposure color-disappearing coloring matter, for example, a triphenylmethane coloring matter, a diphenylmethane coloring matter, an oxazin coloring matter, a xanthene coloring matter, an imino-naphthoquinone coloring matter, an azomethene coloring matter, and an anthraquinone coloring matter can be mentioned.

[0084] The visible light exposure type platemaking layer can be formed by for example applying a photopolymer solution obtained by mixing the photopolymer and the colorant with a solvent, and then drying. As the solvent used for the photopolymer solution, there can be mentioned a solvent which is able to dissolve the photopolymer and has a certain degree of volatility at room temperature. Specifically, there can be mentioned, for example, an alcohol solvent, a ketone solvent, an ester solvent, an ether solvent, a glycol ether solvent, an amide solvent, and a carbonate solvent. As the alcohol solvent, there can be mentioned, for example, ethanol, propanol, and butanol. As the ketone solvent, there can be mentioned, for example, acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, and diethyl ketone. As the ester solvent, there can be mentioned, for example, ethyl acetate, propyl acetate, methyl formate, and ethyl formate. As the ether solvent, there can be mentioned, for example, tetrahydrofuran, and dioxane. As the glycol ether solvent, there can be mentioned, for example, ethyl cellosolve, methyl cellosolve, and butyl cellosolve. As the amide solvent, there can be mentioned, for example, dimethylformamide, and dimethylacetamide. As the carbonate solvent, there can be mentioned, for example, ethylene carbonate, propylene carbonate, diethyl carbonate, and dibutyl carbonate.

[0085] A method for applying the photopolymer solution is not particularly limited, and conventionally well-known methods, such as a rotation application method, a wire bar application method, a dip application method, an air knife application method, a roll coating method, and a blade application method, can be used.

(2) Laser Exposure Type Platemaking Layer

[0086] As the laser exposure type platemaking layer, there can be mainly mentioned, for example, a negative type laser platemaking layer in which a portion irradiated with laser light remains, a positive type laser platemaking layer from which a portion irradiated with laser light is removed, and a photopolymerization type laser platemaking layer which is photopolymerized when irradiated with laser light.

[0087] The negative type laser platemaking layer can be formed by using a solution for forming the negative type laser platemaking layer, the solution obtained by dissolving or suspending, in a suitable solvent, (A) an acid precursor which is decomposed by heat or light to generate acid, (B) an acid-crosslinking compound which is crosslinked by the acid generated by decomposition of the acid precursor (A), (C) an alkali soluble resin, (D) an infrared absorber, and (E) a phenolic hydroxyl-containing compound.

[0088] As the acid precursor (A), there can be mentioned, for example, like an imino phosphate compound, a compound which is decomposed by ultraviolet light, visible light, or heat, thereby generates sulfonic acid. In addition, a compound generally used as a photo-cationic polymerization initiator, a photo-radical polymerization initiator, a photol alterant, etc. also can be used as the acid precursor (A). As the acid-crosslinking compound (B), there can be mentioned, for example, an aromatic compound having at least any one of an alkoxy methyl group and an hydroxyl group, a compound having an N-hydroxymethyl group, an N-alkoxy methyl group, or an N-acyloxy methyl group, and an epoxy compound. As the alkali soluble resin (C), there can be mentioned, for example, a novolak resin, a polymer having a hydroxy aryl group as a side chain of poly(hydroxy styrene), etc.

[0089] As the infrared absorber (D), there can be mentioned, for example, a dye and a pigment which absorb infrared rays with a wavelength of 760 to 1200 nm. Specifically, there can be mentioned, for example, a black pigment, a red pigment, a metallic powder pigment, a phthalocyanine pigment; an azo dye which absorbs infrared rays having the above-mentioned wavelength, an anthraquinone dye, a phthalocyanine dye, and a cyanine dye. As the phenolic hydroxyl-containing compound (E), there can be mentioned, for example, a compound expressed by a general formula (R1-X_n-Ar-$(OH)_m$ (In the formula, R1 is an alkyl group or an alkenyl group having a carbon number of 6 to 32, X is a single bond, O, S, COO, or CONCH, Ar is an aromatic hydrocarbon group, a cycloaliphatic hydrocarbon group, or a heterocycle group, and each of n and m is independently a natural number of 1 to 8.). As such compound, for example, alkylphenols, such as nonylphenol, can be mentioned. For the solution for forming the negative type laser platemaking layer, besides the above-mentioned each component, a plasticizer etc. may also be mixed.

[0090] The positive type laser platemaking layer can be formed by using a solution for forming the positive type laser platemaking layer, the solution obtained by dissolving or suspending (F) an alkali-soluble macromolecule, (G) an alkali-dissolution inhibitor, and (H) a infrared absorber, in a suitable solvent. As the alkali-soluble macromolecule (F), there can be mentioned, for example, a phenol polymer having a phenolic hydroxyl group, such as a phenol resin, a cresol resin, a novolak resin, a pyrogallol resin, and a poly(hydroxystyrene); a sulfonamide group-containing polymer being a polymer in which at least a part of monomeric units has sulfonamide groups; and an active imido group-containing polymer obtained by homopolymerization or copolymerization of monomers having an active imido group, such as an N-(p-toluenesulfonyl) (meta)acrylamide group.

[0091] As the alkali-dissolution inhibitor (G), there can be mentioned, for example, a compound which reacts with the alkali-soluble macromolecule (F) by heating etc. to reduce alkali solubility of the alkali-soluble macromolecule (F). Specifically, for example, a sulfone compound, an ammonium salt, a sulfonium salt, and an amide compound can be mentioned. As a combination of the alkali-soluble macromolecule (F) and the alkali-dissolution inhibitor (G), there can be preferably mentioned a combination of a novolak resin as the alkali soluble macromolecule (F) and a cyanine dye, a kind of a sulfone compound, as the alkali-dissolution inhibitor (G). As the infrared absorber (H), there can be mentioned, for example, a coloring matter, a dye, and a pigment which have an absorption region in an infrared region with a wavelength range of 750 to 1200 nm and have a light-heat conversion ability, such as a squarylium coloring matter, a pyrylium coloring matter, a carbon black, an insoluble azo dye, and an anthraquinone dye.

[0092] The photopolymerization type laser platemaking layer can be formed by using a solution for forming the photopolymerization type laser platemaking layer, the solution containing (I) a vinyl polymer compound having an ethylene unsaturated bond at a molecular end. For the solution for forming the photopolymerization type laser platemaking layer, (J) a photopolymerization initiator, (K) a sensitizer, etc. can be mixed, as needed. As the vinyl polymer compound (I), there can be mentioned, for example, an ethylene unsaturated carboxylic acid polyvalent ester which is an ester of an ethylene unsaturated carboxylic acid, such as (meta)acrylic acid, itaconic acid, and maleic acid, and an aliphatic polyhydric alcohol; a methylenebis(meta)acrylamide composed of the ethylene unsaturated carboxylic acid and a polyvalent amine; and an ethylene unsaturated carboxylic acid polyvalent amide, such as a xylylene(meta)acrylamide. As the vinyl polymer compound (I), there can be further mentioned, an aromatic vinyl compound, such as a styrene and an α-methylstyrene; and an ethylene unsaturated carboxylic-acid monoester, such as methyl (meta)acrylate and ethyl (meta)acrylate. As the photopolymerization initiator (J), a photopolymerization initiator which is usually used for photopolymerization of vinyl monomers can be used. As the sensitizer (K), there can be mentioned, for example, a titanocene compound, a triazine compound, a benzophenone compound, a benzimidazole compound, a cyanine dye, a merocyanine dye, a xanthene dye, and a coumarin dye.

[0093] The solvent and the applying method which are mentioned above for the photopolymer solution can be employed for solvents to be used for the solution for forming the negative type laser platemaking layer, the solution for forming the positive type laser platemaking layer, and the solution for forming the photopolymerization type laser platemaking layer, and applying methods of the solution for forming the negative type laser platemaking layer, the solution for forming the positive type laser platemaking layer, and the solution for forming the photopolymerization type laser platemaking layer. Note that, when the photopolymerization type laser platemaking layer is formed, it is preferable that, by using a silicone compound having a reactant functional group, such as a partially decomposed type silane compound obtained by partially decomposing a silane compound by water, alcohol, or carboxylic acid, a treatment is in advance provided to a surface-roughening treatment surface of the support for lithographic printing plates, since adhesiveness of the support and the photopolymerization type laser platemaking layer is improved.

<Mat layer>

[0094] A mat layer may be provided on the surface of the thus-provided photosensitive layer in order to shorten the vacuuming time at the time of contact exposure by using a vacuum printing frame and to prevent halation. Specifically, the methods of providing a mat layer, and the method of thermal deposition of solid powders can be mentioned.

<Back coat layer>

[0095] For the lithographic printing plate original plate obtained as mentioned above, a coating layer comprising an organic macromolecular compound (hereinafter, referred to as "back coat layer") may be prepared as necessary on the back side of the lithographic printing plate original plate (a side on which the photosensitive layer is not provided) so that the photosensitive layer is not damaged even if the lithographic printing plate original plates are piled up. As a principal component of the back coat layer, it is preferable to use at least one kind of resin having a glass transition point of 20 °C or more and chosen from a group including saturated copolymerization polyester resin, phenoxy resin, polyvinyl acetal resin, and vinylidene chloride copolymerization resin.

[0096] The saturated copolymerization polyester resin is composed of a dicarboxylic acid unit and a diol unit. As the dicarboxylic acid unit, there can be mentioned, for example, aromatic dicarboxylic acid such as phthalic acid, terephthalic acid, isophthalic acid, tetrabromophthalic acid, and tetrachlorophthalic acid; and saturated aliphatic dicarboxylic acid such as adipic acid, azelaic acid, succinic acid, oxalic acid, suberic acid, sebacic acid, malonic acid, and 1,4-cyclohexanedicarboxylic acid.

[0097] Furthermore, the back coat layer may suitably include a dye and a pigment for coloring, a silane coupling agent for improving adhesion to the support, a diazo resin comprising a diazonium salt, an organic phosphonic acid, an organic phosphorus acid, a cationic polymer, a wax usually used as a sliding agent, a higher fatty acid, a higher fatty acid amide, a silicone compound comprising dimethyl siloxane, a denatured dimethyl siloxane, polyethylene powders, etc.

[0098] It is only necessary that a thickness of the back coat layer has a degree where the photosensitive layer cannot be easily damaged even without a backing board, and preferably 0.01 to 8 μm. If the thickness is less than 0.01 μm, it is difficult to prevent a scratch of the photosensitive layer when the lithographic printing plate original plates are piled up and handled. Meanwhile, if the thickness is more than 8 μm, due to medicine used around the lithographic printing plate, sometimes the back coat layer swells to change the thickness during printing and thereby printing pressure changes to degrade a printing characteristics.

[0099] Various methods can be used as methods of providing the back coat layer in the back side of the lithographic printing plate original plate. There can be mentioned, for example, a method where the above-mentioned components for the back coat layer are dissolved in a suitable solvent to make a solution and applied, or to make into an emulsification dispersion solution and applied, and then dried; a method where what is beforehand formed in a film form and the lithographic printing plate original plate are pasted together with adhesive or heat; and a method where a molten coat is formed with a melting extruder and stuck to the lithographic printing plate original plate. A most preferable method for ensuring a preferable thickness is the method where the components for the back coat layer is dissolved in a suitable solvent to make a solution and applied, then dried.

[0100] In the production of the lithographic printing plate original plate, either the back coat layer on the back side and the photosensitive layer on the front side maybe provided first on the support, and both the layers may also be provided simultaneously,

[0101] The lithographic printing plate is obtained by, as necessary, cutting the thus-obtained lithographic printing plate original plate in a suitable size, and then exposing, developing, and photoengraving the original plate. In the case of the lithographic printing plate original plate in which the visible light exposure type platemaking layer (photosensitive platemaking layer) is provided, the lithographic printing plate original plate is exposed by layering transparent films in which printing pictures are formed and irradiating ordinary visible light, and subsequently is developed, thereby can be photoengraved. In the case of the lithographic printing plate original plate in which the laser exposure type platemaking layer is provided, the lithographic printing plate original plate is exposed by irradiating various laser lights to write a printing image directly, and subsequently is developed, thereby can be photoengraved.

[0102] As mentioned above, the example to apply the present invention to the production method for producing the support for lithographic printing plates was explained, and the present invention is also applicable to other technical fields including a process in which the electrolytic surface-roughening treatment is performed to the surface of a metal plate.

[Example]

[0103] Next, the present invention will be explained in more detail by Examples, but should not be limited to the following Examples.

[0104] With reference to Fig. 2, an explanation is given. Fig. 2 is a diagram showing an example of an apparatus which is used for the electrolytic surface-roughening method according to the present invention. An electrolytic surface-roughening treatment by an alternating current with using a nitric acid solution was carried out in a container 200 having a size of 100 × 100 × 100 mm.

[0105] In the apparatus shown in Fig. 2, a concentration of a nitric acid solution 210 was set to 10 g/l, and a solution temperature was set to 35 °C, then a nitrogen purge was performed by injecting nitrogen gas 220 into a nitric acid solution 210. A concentration of dissolved oxygen in the nitric acid solution 210 was adjusted by the nitrogen purge. The concentration of dissolved oxygen was measured by a dissolved oxygen analyzer (made by Central Kagaku Corp).

[0106] An aluminum support body 230 and a carbon electrode 240 were disposed such that each plane would face each other in the nitric acid solution 210. Each of the aluminum support body 230 and the carbon electrode 240 was connected to an alternating-current power supply 250. A distance between the aluminum support body 230 and the carbon electrode 240 was set to 10 mm. Moreover, for the aluminum support body 230, A1050 is used as an aluminum material.

[0107] With a state where 1% of the nitric acid solution 210 is stationary, an electrolytic surface-roughening treatment of the aluminum support body 230 was carried out. A current density in alternating current electrolysis was set to 35 A/dm^2, and a total quantity of electricity was set to 240 C/dm^2. At this time, the electrolytic surface-roughening treatment was performed with changing the concentration of the dissolved oxygen in the nitric acid solution 210 as a parameter. The change in dissolved oxygen was performed by the nitrogen purge as mentioned above.

[0108] Uniformity of pits was evaluated by performing SEM photography of a surface-roughened surface of the aluminum support body 230 to observe the surface. The evaluation results are shown in Table 1. Fig. 3 and Fig. 4 show SEM photographs taken at this time. Fig. 3 shows a SEM photograph of a surface of the aluminum support body to which the electrolytic surface-roughening treatment was given without removing dissolved oxygen in the nitric acid solution 210. Fig. 4 shows a SEM photograph of a surface of the aluminum support body to which the electrolytic surface-roughening treatment was given at a dissolved oxygen concentration of 3 mg/l, with removing dissolved oxygen in the nitric acid solution 21 fl.

[Table 1]

	Removal of Dissolved Oxygen	Concentration of Dissolved Oxygen (mg/l)	Average Diameter of Pits (μm)	Pit Density (10,000 pits/mm^2)	Pit Uniformity
Comparative Example	w/o	8	5.6	1.5	B
Example 1	w/	1 or less	3.0	2.0	A
Example 2	w/	3	3.4	1.8	A-AB
Example 3	w/	6	3.9	1.6	AB- B

[0109] The pit average diameter and the pit density were calculated by analyzing the 174 × 254 μm SEM photographs. As an evaluation level of the pit uniformity, a following four-grade evaluation on the basis of Comparative Example was applied.

A: Excellent in pit uniformity
A - AB: Good in pit uniformity
AB - B: Satisfactory in pit uniformity
B: Fair in pit uniformity

[0110] As shown in Table 1, it is preferable that electrolytic surface-roughening treatment is performed in the nitric acid solution with a dissolved oxygen concentration of 6 mg/l or less. Thereby, an aluminum support body having a smaller average diameter of pits, a higher pit density, and a better uniformity of pits can be manufactured.

[0111] Moreover, it is more preferable that the electrolytic surface-roughening treatment is performed in the nitric acid solution with a dissolved oxygen concentration of 3 mg/l or less, and it is most preferable that the electrolytic surface-roughening treatment is performed in the nitric acid solution with a dissolved oxygen concentration of 1 mg/l or less. Thereby, an aluminum support body having a smaller average diameter of pits, a still higher pit density, and a still better uniformity of pits can be manufactured.

[0112] Here, Fig. 3 and Fig. 4 are compared. Fig. 3 shows a SEM photograph of a surface of the aluminum support body manufactured under conditions of Comparative Example in Table 1, and Fig. 4 shows a SEM photograph of a surface of the aluminum support body manufactured under conditions of Example 2 in Table 1.

[0113] From Fig. 3 and Fig. 4, it is apparent that the aluminum support body manufactured under the conditions of Example 2 has a smaller average diameter of pits, a higher pit density, and a better uniformity of pits than the aluminum support body manufactured under the conditions of Comparative Example.

[Application as Support for Lithographic Printing Plate]

(Desmut Treatment in Acidic Solution)

[0114] The desmut treatment was performed for 5 seconds by spraying an aqueous solution with a sulfuric acid concentration of 170 g/L, an aluminum ion concentration of 5 g/L, and a temperature of 50 °C, from a spray pipe, on an aluminum plate obtained by the surface-roughening treatment. As the sulfuric acid solution, a waste in the anodizing treatment step mentioned later was used.

[0115] Then, the solution was drained off by a nip roller. After draining off the solution, the anodizing treatment step was applied without performing a water-washing treatment.

(Anodizing Treatment)

[0116] As the electrolyte, used was an electrolyte (a solution temperature of 50 °C) in which aluminum sulfate was dissolved in a 170 g/L sulfuric acid solution so that an aluminum ion concentration was 5g/L. Anodizing treatment was performed so that an average current density during an anode reaction of the aluminum plate would become 15 A/dm^2, and a final amount of an oxide film was 2.7 g/m^2.

[0117] Then, the solution was drained off by a nip roller, and a water-washing treatment is carried out for 5 seconds by using a spray pipe having a spray tip from which injection water was spread fan-like, and furthermore the solution was drained off by a nip roller.

(Hydrophilization Treatment)

[0118] The aluminum plate was soaked in a sodium silicate solution of 1% by mass (a solution temperature of 20 °C) for 10 seconds. An amount of Si on a surface of the aluminum plate measured by a fluorescent X-ray analysis apparatus was 3.5 mg/m^2. Then, the solution was drained off by a nip roller, and a water-washing treatment was carried out for 5 seconds by using a spray pipe having a spray tip from which injection water was spread fan-like, and furthermore the solution was drained off by a nip roller. Furthermore, by drying by blowing an air flow of 90 °C for 10 seconds, a support for lithographic printing plates was obtained.

Production of Lithographic Printing Plate Original Plate

[0119] A thermal positive type image recording layer was provided to each support of the above-obtained lithographic printing plates as follows to obtain a lithographic printing plate original plate. It is note that, before providing the image recording layer, an undercoating layer was provided as described later.

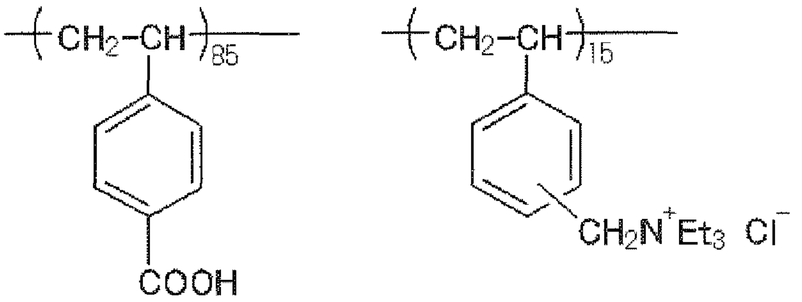
[0120] An undercoating solution having the following composition was applied on the support for lithographic printing plates and then dried at 80 °C for 15 seconds to form a coating film of the undercoating layer. After drying, a coating amount of the coating film was 15 mg/m^2.

<Composition of Undercoating Solution>

[0121]

- Macromolecular Compound below: 0.3 g
- Methanol: 100g
- Water: 1g

[Chemical Formula 6]



Molecular Weight: 28,000

[0122] Furthermore, an application solution for thermal layers having a following composition was prepared, then the application solution for thermal layers was applied to the support for lithographic printing plates to which the undercoating layer had been prepared so that an application amount after drying (an application amount for a thermal layer) would be 1.8 g/m^2, and then dried to form a thermal layer (the thermal positive type image recording layer), whereby the lithographic printing plate original plate was obtained.

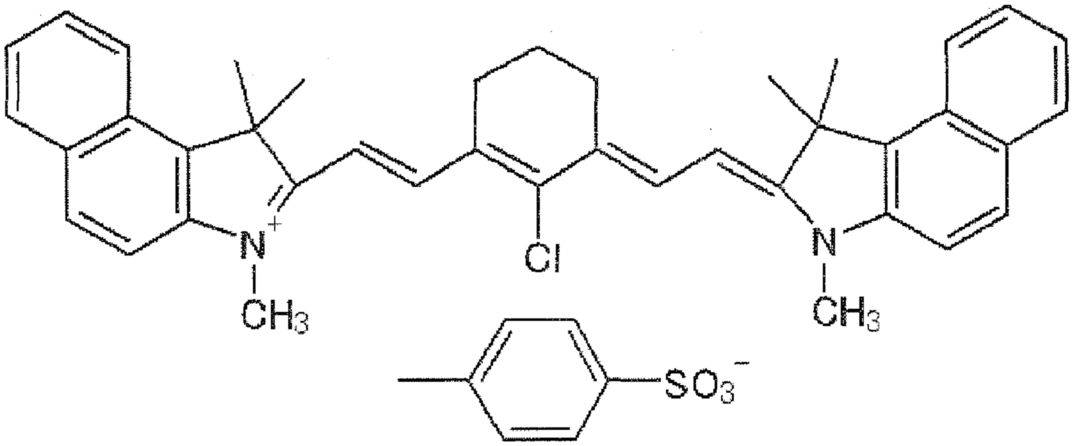
<Composition of Application Solution for Thermal Layer>

[0123]

- Novolak resin (m-cresol/p-cresol = 60/40, weight average molecular weight: 7,000, containing unreacted cresol of 0.5% by mass): 0.90 g
- Copolymer of ethyl methacrylate/isobutyl methacrylate/methacrylic acid (molar ratio 35/35/30): 0.10 g
- Cyanine dye A represented by a following structural formula: 0.1 g
- Tetrahydrophthalic anhydride: 0.05 g
- ρ-toluenesulfonic acid: 0.002 g
- Ethyl Violet having 6-hydroxy-β-naphthalenesulfonic acid as a counter ion: 0.02 g
- Fluorine surface active agent (Megafac F-780F, produced by Dainippon Ink and Chemicals Inc., a solid content of 30% by mass): 0.0045 g (solid content conversion)
- Fluorine surface active agent (Megafac F-781F, produced by Dainippon Ink and Chemicals Inc., a solid content of 100% by mass): 0.035 g
- Methyl ethyl ketone: 12 g

[Chemical Formula 7]

Cyanine Dye A



Evaluation of Lithographic Printing Plate Original Plate

[0124] Sensitivity of exposure and development and adhesion to an upper layer were evaluated for the obtained lithographic printing plate original plate.

(1) Evaluation of Sensitivity of Exposure and Development

[0125] Writing was performed in image form with respect to the obtained lithographic printing plate original plate at a drum rotation speed of 150 rpm and a beam intensity of 10 W, using TrendSetter manufactured by Creo Inc.. Then, by using PS processor 940H manufactured by Fuji Photo Film Co., Ltd. in which an alkaline development solution with a following composition had been prepared, a development was performed for a developing time of 20 seconds with maintaining a solution temperature at 30 °C, whereby a lithographic printing plate was obtained.

[0126] As a result, sensitivity of the lithographic printing plate original plate produced under any of conditions of the above Examples 1 to 3 and the above Comparative Example in Table 1 was good.

[0127] Composition of the alkaline development solution which was used for the sensitivity evaluation of exposure and development is shown below.

<Composition of Akaline Development Solution>

[0128]

- D-sorbitol: 2.5% by mass
- Sodium hydroxide: 0.85% by mass
- Polyethylene glycol lauryl ether (weight average molecular weight: 1.000): 0.5% by mass
- Water: 96.15% by mass

(2) Evaluation of Adhesion to Upper Layer (Evaluation of Printing Durability)

[0129] Next, an evaluation of adhesion to an upper layer was performed. Here, the evaluation of adhesion to an upper layer is to evaluate adhesion of a surface of the aluminum support body, on which pits were formed, to a layer which is formed on the surface of the aluminum support body. Here, the adhesion to the upper layer was decided by evaluating printing durability. An evaluation of the printing durability was performed by evaluating the printable number of layers under each condition (Examples 1 to 3 and Comparative Example in Table 1), and was expressed by an index when the printable number in Comparative Example was made 100%.

[Printing Durability Test Condition]

[0130] Printing was performed with respect to the obtained lithographic printing plate, by using a LITHRONE printing machine manufactured by KOMORI Corporation and a black ink, DIC-GEOS (N) made by Dainippon Ink and Chemicals Inc., and then a usual printing durability was evaluated by the number of printed layers at a time when it was recognized by visual inspection that a solid image density began to become lighter.

[Test Result]

[0131] Table 2 shows test results (the number of printable layers in the case where the dissolved oxygen treatment was not performed was made an index of 100). Each of Examples 1 to 3 and Comparative Example in this table is a sample to which electrolytic surface-roughening treatment is given under the same conditions as in each of Examples 1 to 3 and Comparative Example in Table 1.

[Table 2]

	Removal of Dissolved Oxygen	Concentration of Dissolved Oxygen (mg/l)	Pit Uniformity	Printing Durability
Comparative Example	w/o	8	B	100%
Example 1	w/	1 or less	A	116%
Example 2	w/	3	A-AB	110%
Example 3	w/	6	AB- B	103%

[0132] As shown in Table 2, printing durability in each of Examples 1 to 3 was more improved than that in Comparative Example. It is presumed that uniformity of the pits was improved by reducing a dissolved oxygen concentration in a nitric acid solution, and accordingly adhesion to an upper layer became better, whereby printing durability was improved. Thereby, it was proved that, with conveying an aluminum web W into an acidic electrolyte, the alternating current electrolysis treatment is continuously performed by a frequency wave current, whereby pits which are uniform in diameter can be formed, thus, printing durability can be effectively improved.

[0133] Particularly, as seen from results of Examples 1 to 3, a dissolved oxygen concentration of 1 mg/l or less is most effective. Therefore, it is proved that removal of dissolved oxygen in the nitric acid solution contributes to uniformity of the pits, in other words, printing durability.

[0134] On the other hand, it was proved that, in Comparative Example in which dissolved oxygen was not removed, printing durability decreases.

Claims

1. A method for roughening a surface of an aluminum support body, **characterized in that** an electrolysis treatment is provided to the aluminum support body in an acidic solution having a dissolved oxygen concentration of 6.0 mg/l or less.

2. The method for roughening a surface of an aluminum support body according to Claim 1, wherein the electrolysis treatment is alternating current electrolysis treatment, or direct current electrolysis treatment by an anode reaction.

3. The method for roughening the surface of an aluminum support body according to Claim 1 or Claim 2, **characterized in that** the dissolved oxygen concentration is adjusted to be 6.0 mg/l or less by removing oxygen contained in the acidic solution by any of methods of film degassing, a nitrogen purge, and a pressure reduction.

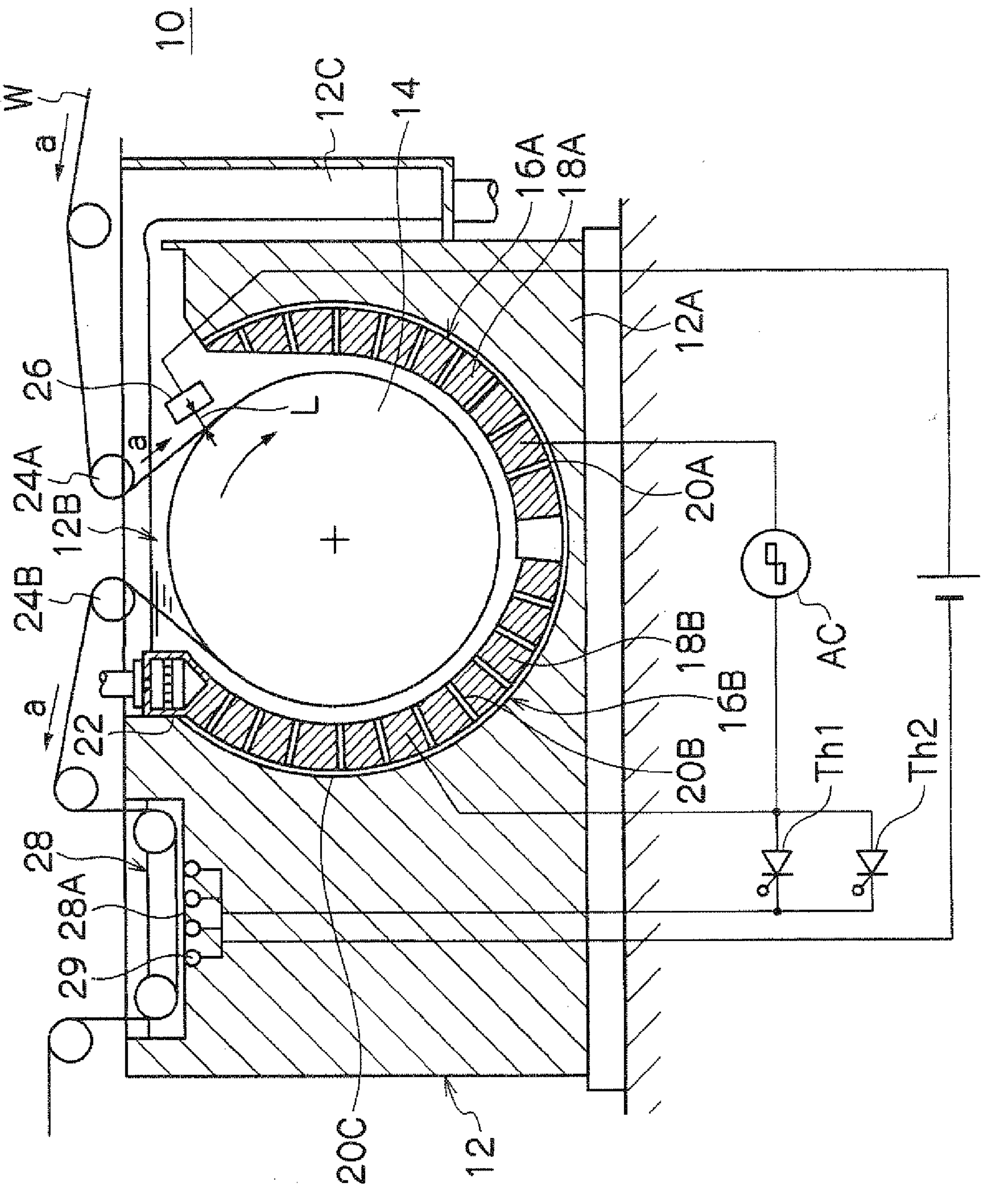
4. The method for roughening the surface of an aluminum support body according to any one of Claims 1 to 3, **characterized in that** the aluminum support body is a support for lithographic printing plates.

5. A surface-roughened aluminum support body obtainable by a method as claimed in any one of claims 1 to 3.

6. A method for producing a lithographic printing plate original plate, the method comprising an electrolytic surface-roughening treatment step to perform an electrolytic surface-roughening treatment of an aluminum support body, **characterized in that** the electrolytic surface-roughening treatment of the aluminum support body is carried out by a method as claimed in any one of claims 1 to 3.

7. A lithographic printing plate original plate obtainable by a production method as claimed in claim 6.

FIG. 1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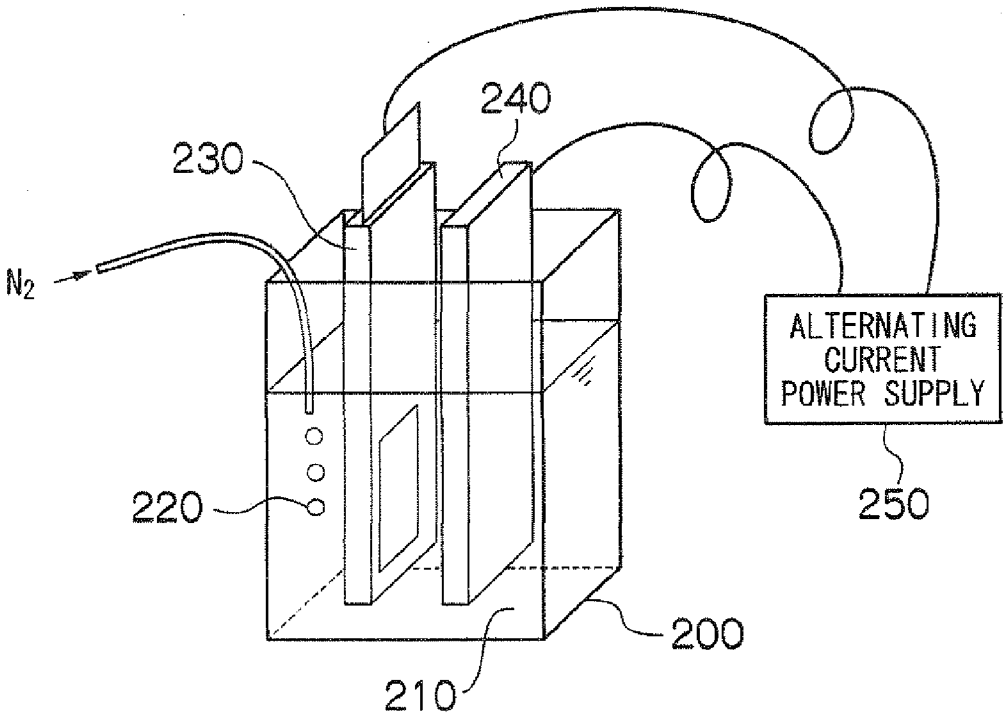
W
a
12C
14
16A
18A
12A
26
L
24A
a
12B
20A
24B
AC
18B
16B
a
22
20B
Th1
Th2
28
28A
29
20C
12

FIG. 2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230
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ALTERNATING CURRENT POWER SUPPLY
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220
200
210

FIG. 3

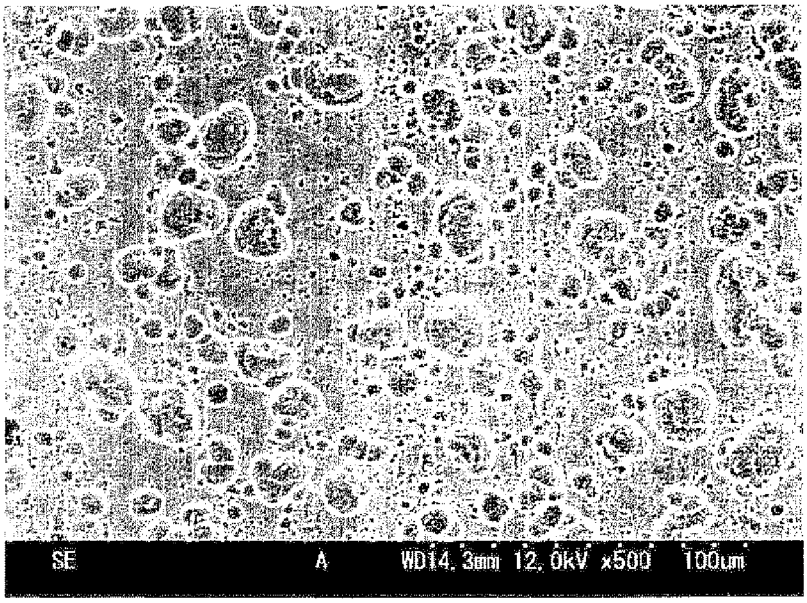
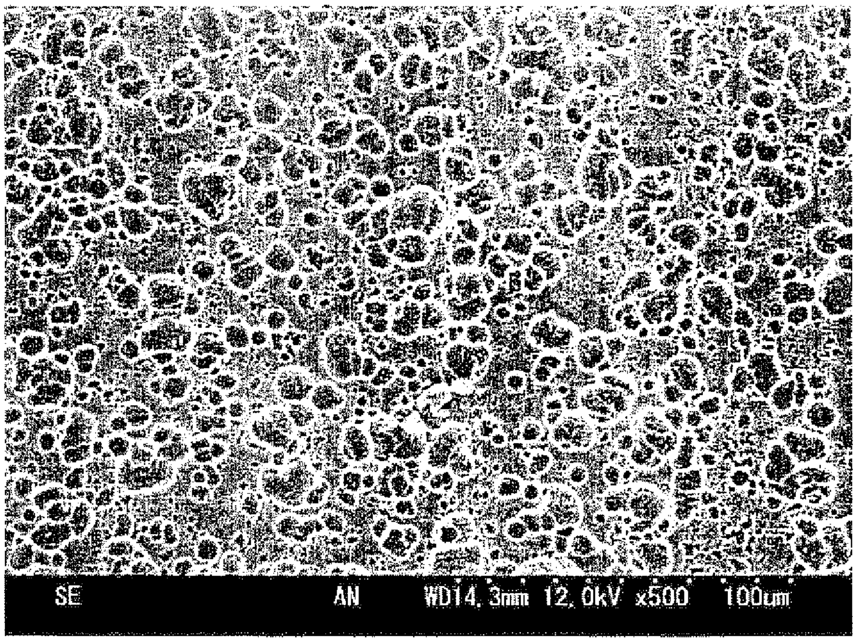

SE
A
WD14.3mm 12.0kV x500
100um

FIG. 4



REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2614744 B **[0008] [0009]**