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(54) Method of manufacturing lithographic printing plate support

(57) A method of manufacturing a lithographic printing plate support having a step of subjecting an aluminum plate to an electrochemical graining treatment in which alternating current is passed through the aluminum plate in an aqueous solution containing at least chloride ion and nitrate ion so that total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2. By this method, a lithographic printing plate support which makes it possible to obtain a presensitized plate having both an excellent scumming resistance and a good press life by a single electrochemical graining treatment.

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Description

[0001] The entire contents of documents cited in this specification are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a method of manufacturing a lithographic printing plate support. More specifically, the invention relates to a method of manufacturing a lithographic printing plate support used for a presensitized plate which has both an excellent scumming resistance and a good press life.

[0003] Lithography is a printing process which makes use of a nature that water and oil are essentially unmixable with each other. On the printing surface of a lithographic printing plate used in this process, areas that receive water and repel an oil-based ink (hereinafter referred to as "non-image areas") and areas that repel water and receive an oil-based ink (hereinafter referred to as "image areas") are provided.

[0004] The surface of an aluminum support for lithographic printing plates used for a lithographic printing plate (hereinafter also referred to simply as "a lithographic printing plate support") is required to have various conflicting characteristics. For instance, it should be excellent in water wettability and water receptivity because of being so used as to carry non-image areas and at the same time should give good adhesion to the image recording layer formed on it. If the surface of a lithographic printing plate support exhibits too low a water wettability, non-image areas are to be stained with ink upon printing, resulting in generation of dirt on a blanket cylinder or even so-called scumming, that is to say, the scumming resistance is reduced. In addition, if the water receptivity of the surface is too low, certain inconveniences will arise at the time of printing, including plugging of shadows, unless fountain solution is increased in amount. On the other hand, if the adhesion between the support surface and the image recording layer is too poor, the image recording layer is liable to peel off and accordingly the durability (press life) is decreased during printing of a large number of printed sheets.

[0005] In fact, the surface of a lithographic printing plate support is subjected to graining treatment and other surface treatments in order to improve various characteristics such as scumming resistance and press life. Examples of a known graining treatment include a mechanical graining treatment such as ball graining, brush graining, wire graining, and blast graining; an electrochemical graining treatment in which alternating current is passed through an aluminum plate immersed in an acidic solution; chemical etching (chemical graining treatment); and a combination thereof.

[0006] Among such graining treatments, the electrochemical graining treatment as above provides recesses (pits) with an average diameter of 1 to 5 μm uniformly through the entire surface of an aluminum plate, with an aqueous solution containing nitric acid being used as the acidic solution. If an aqueous solution containing hydrochloric acid is used as the acidic solution, pits with an average diameter of 0.01 to 0.5 μm are formed uniformly through the entire surface of an aluminum plate.

[0007] In the case where an aluminum plate is initially subjected to an electrochemical graining treatment using an aqueous solution containing nitric acid as the acidic solution and then to an electrochemical graining treatment using an aqueous solution containing hydrochloric acid as the acidic solution, the aluminum plate will have asperities formed through its entire surface, in which pits with an average diameter of 0.01 to 0.5 μm are superimposed on pits with an average diameter of 1 to 5 μm. A lithographic printing plate in which an aluminum plate of such a surface profile as above is used as the lithographic printing plate support is excellent in both scumming resistance and press life.

[0008] In addition, JP 48-28123 B (the term "JP XX-XXXXXX B" as used herein means an "examined Japanese patent publication") describes a method of manufacturing an offset printing plate which includes a step of graining an aluminum plate or an aluminum alloy plate by alternating current electrolysis in a solution containing 1 to 3% of hydrochloric acid and nitric acid at a current density exceeding 10 A/dm^2, a step of slightly etching in an aqueous alkali solution, and a step of performing anodizing treatment to form an anodized layer having a thickness of not more than 5μ.

SUMMARY OF THE INVENTION

[0009] In the former case, however, it is necessary to perform two kinds of electrochemical graining treatments, an electrochemical graining treatment using an aqueous solution containing nitric acid as the acidic solution, and then an electrochemical graining treatment using an aqueous solution containing hydrochloric acid as the acidic solution. In other words, manufacturing of a lithographic printing plate support needs an increased number of processes and is more complicated.

[0010] As for the latter case, namely the method described in JP 48-28123 B, the present inventors reviewed it to find that the disclosed techniques provide pits with an average diameter of about 1 to 5 μm and coarse recesses with an average diameter exceeding 10 μm on the aluminum plate surface in a mixed manner and that a lithographic printing plate in which an aluminum plate of such a surface profile is used as the lithographic printing plate support has neither an adequate scumming resistance nor press life.

[0011] It is an object of the present invention to provide a method of manufacturing a lithographic printing plate support which makes it possible to obtain a presensitized plate having both an excellent scumming resistance and a good press life by a single electrochemical graining treatment.

[0012] In order to achieve the above and other objects, the present inventors have intensively studied to finally find out that, if an aluminum plate is subjected to an electrochemical graining treatment, in which alternating current is passed through the aluminum plate in an aqueous solution containing at least chloride ion and nitrate ion so that the total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2, so as to obtain a lithographic printing plate support, a presensitized plate in which the lithographic printing plate support is used has both an excellent scumming resistance and a good press life, even though the aluminum plate is subjected to one electrochemical graining treatment only.

[0013] According to the preset invention, there are provided the following (1) to (6).

(1) A method of manufacturing a lithographic printing plate support comprising a step of subjecting an aluminum plate to an electrochemical graining treatment in which alternating current is passed through the aluminum plate in an aqueous solution containing at least chloride ion and nitrate ion so that total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2.

(2) The method of manufacturing a lithographic printing plate support according to (1) as above, wherein the aqueous solution contains hydrochloric acid and nitric acid.

(3) The method of manufacturing a lithographic printing plate support according to (1) or (2) as above, wherein the aqueous solution has a chloride ion concentration of 3 g/L or more and a nitrate ion concentration of 0.50 g/L or more.

(4) The method of manufacturing a lithographic printing plate support according to any one of (1) to (3) as above, wherein the aqueous solution has a pH of 0.8 or less.

(5) The method of manufacturing a lithographic printing plate support according to any one of (1) to (4) as above, wherein the aqueous solution contains 2 g/L or more of aluminum ions.

(6) The method of manufacturing a lithographic printing plate support according to any one of (1) to (5) as above, wherein the aluminum plate has a pattern of recessed and protruded portions provided on its surface.

[0014] As will be described below, according to the present invention, the lithographic printing plate support can be obtained that is used for a presensitized plate which has both an excellent scumming resistance and a good press life when made into a lithographic printing plate. Moreover, the lithographic printing plate support used for a presensitized plate which has both an excellent scumming resistance and a good press life when made into a lithographic printing plate can be obtained by subjecting an aluminum plate to a single electrochemical graining treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] In the accompanying drawings:

FIG. 1 is a schematic cross-sectional view of an apparatus for rinsing with a free-falling curtain of water that is used for rinsing in the method of manufacturing a lithographic printing plate support according to the present invention;

FIG. 2 is a schematic cross-sectional view of an aluminum plate provided with asperities, in which pits with an average diameter of 0.01 to 0.5 μm are superimposed on pits with an average diameter of 1 to 5 μm;

FIG. 3 is a graph showing an example of an alternating current waveform that is used in electrochemical graining treatment in the method of manufacturing a lithographic printing plate support according to the present invention;

FIG. 4 is a side view of a radial electrolytic cell that is used to carry out electrochemical graining treatment with alternating current in the method of manufacturing a lithographic printing plate support according to the present invention;

FIG. 5 is a schematic view of an anodizing apparatus that is used in anodizing treatment in the method of manufacturing a lithographic printing plate support according to the present invention: and

FIG. 6 is a side view conceptually showing processes of mechanical graining treatment in the method of manufacturing a lithographic printing plate support according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention will be described below in detail.

[Method of Manufacturing Lithographic Printing Plate Support]

<Aluminum Plate (Rolled Aluminum)>

[0017] A known aluminum plate can be used to obtain the lithographic printing plate support of the present invention. The aluminum plate used in the present invention is made of a dimensionally stable metal composed primarily of aluminum; that is, aluminum or aluminum alloy. Aside from plates of pure aluminum, alloy plates composed primarily of aluminum and containing small amounts of other elements can also be used.

[0018] In the present specification, various plates made of such aluminum or aluminum alloy as above are referred to generically as "aluminum plate." Other elements which may be present in the aluminum alloy include silicon, iron, copper, manganese, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of other elements in the alloy is not more than 10 wt%.

[0019] Aluminum plates that are suitable for use in the present invention are not specified here as to composition, but include plates of known materials that appear in the 4th edition of Aluminum Handbook published in 1990 by the Light Metal Association (Japan), such as aluminum alloys bearing the designations JIS A1050, JIS A1100, JIS A1070, JIS A3004 and International Alloy Designation 3103A, with the last two materials being manganese-containing aluminum-manganese-based aluminum alloys. For increased tensile strength, it is preferable to use aluminum-magnesium alloys and aluminum-manganese-magnesium alloys (e.g. JIS A3005) composed of the above aluminum alloys to which at least 0.1 wt% of magnesium has been added. Aluminum-zirconium alloys and aluminum-silicon alloys which contain zirconium and silicon, respectively, may also be used. Use can also be made of aluminum-magnesium-silicon alloys.

[0020] An aluminum plate obtained by rolling a UBC (used beverage can) ingot into which a used aluminum beverage can in a molten state is formed is also usable.

[0021] The Cu content in the aluminum plate is preferably 0.00 wt% or more, more preferably at least 0.01 wt% and even more preferably at least 0.02 wt% but is preferably 0.15 wt% or less, more preferably 0.11 wt% or less and even more preferably 0.03 wt% or less. An aluminum plate containing 0.07 to 0.09 wt% of Si, 0.20 to 0.29 wt% of Fe, not more than 0.03 wt% of Cu, not more than 0.01 wt% of Mn, not more than 0.01 wt% of Mg, not more than 0.01 wt% of Cr, not more than 0.01 wt% of Zn, not more than 0.02 wt% of Ti and not less than 99.5 wt% of Al is particularly preferred.

[0022] The present applicant has disclosed related art concerning JIS 1050 materials in JP 59-153861 A (the term "JP XX-XXXXXX A" as used herein means an "unexamined published Japanese patent application"), JP 61-51395 A, JP 62-146694 A, JP 60-215725 A, JP 60-215726 A, JP 60-215727 A, JP 60-216728 A, JP 61-272367 A, JP 58-11759 A, JP 58-42493 A, JP 58-221254 A, JP 62-148295 A, JP 4-254545 A, JP 4-165041 A, JP 3-68939 B, JP 3-234594 A, JP 1-47545 B and JP 62-140894 A. The art described in JP 1-35910 B and JP 55-28874 B is also known.

[0023] This applicant has also disclosed related art concerning JIS 1070 materials in JP 7-81264 A, JP 7-305133 A, JP 8-49034 A, JP 8-73974 A, JP 8-108659 A and JP 8-92679 A.

[0024] In addition, this applicant has disclosed related art concerning aluminum-magnesium alloys in JP 62-5080 B, JP 63-60823 B, JP 3-61753 B, JP 60-203496 A, JP 60-203497 A, JP 3-11635 B, JP 61-274993 A, JP 62-23794 A, JP 63-47347 A, JP 63-47348 A, JP 63-47349 A, JP 64-1293 A, JP 63-135294 A, JP 63-87288 A, JP 4-73392 B, JP 7-100844 B, JP 62-149856 A, JP 4-73394 B, JP 62-181191 A, JP 5-76530 B, JP 63-30294 A and JP 6-37116 B. The related art is disclosed also in JP 2-215599 A, JP 61-201747 A, and so forth.

[0025] This applicant has disclosed related art concerning aluminum-manganese alloys in JP 60-230951 A, JP 1-306288 A and JP 2-293189 A. The related art is disclosed also in JP 54-42284 B, JP 4-19290 B, JP 4-19291 B, JP 4-19292 B, JP 61-35995 A, JP 64-51992 A, JP 4-226394 A, US 5,009,722, US 5,028,276, and so forth.

[0026] The present applicant has disclosed related art concerning aluminum-manganese-magnesium alloys in JP 62-86143 A and JP 3-222796 A. The related art is disclosed also in JP 63-60824 B, JP 60-63346 A, JP 60-63347 A, JP 1-293350 A, EP 223,737, US 4,818,300, GB 1,222,777, and so forth.

[0027] Also, this applicant has disclosed related art concerning aluminum-zirconium alloys in JP 63-15978 B and JP 61-51395 A. The related art is disclosed also in JP 63-143234 A, JP 63-143235 A, and so forth.

[0028] Aluminum-magnesium-silicon alloys are described in GB 1,421,710, and so forth.

[0029] The aluminum alloy may be rendered into plate by the following method, for example. An aluminum alloy melt that has been adjusted to a given alloying ingredient content is initially subjected to cleaning treatment by an ordinary method, and then is cast. Cleaning treatment, which is carried out to remove hydrogen and other unnecessary gases from the melt, typically involves flux treatment; degassing treatment using argon gas, chlorine gas or the like; filtering treatment using, for example, what is referred to as a rigid media filter (e.g., ceramic tube filters, ceramic foam filters), a filter that employs a filter medium such as alumina flakes or alumina balls, or a glass cloth filter; or a combination of degassing treatment and filtering treatment.

[0030] Cleaning treatment is preferably carried out to prevent defects due to foreign matter such as nonmetallic inclusions and oxides in the melt, and defects due to dissolved gases in the melt. The filtration of melts is described in, for example, JP 6-57432 A, JP 3-162530 A, JP 5-140659 A, JP 4-231425 A, JP 4-276031 A, JP 5-311261 A, and JP

6-136466 A. The degassing of melts is described in, for example, JP 5-51659 A and JP 5-49148 U. The present applicant discloses related art concerning the degassing of melts in JP 7-40017 A.

[0031] Next, the melt that has been subjected to cleaning treatment as described above is cast. Casting processes include those which use a stationary mold, such as direct chill casting, and those which use a driven mold, such as continuous casting.

[0032] In direct chill casting, the melt is solidified at a cooling speed of 0.5 to 30°C per second. At less than 0.5°C/sec, many coarse intermetallic compounds may be formed. When direct chill casting is carried out, an ingot having a thickness of 300 to 800 mm can be obtained. If necessary, this ingot is scalped by a conventional method, generally removing 1 to 30 mm, and preferably 1 to 10 mm, of material from the surface. The ingot may also be optionally soaked, either before or after scalping. In the case where soaking is carried out, the ingot is heat treated at 450 to 620°C for 1 to 48 hours to prevent the coarsening of intermetallic compounds. The effects of soaking treatment may be inadequate if heat treatment is shorter than one hour. If soaking treatment is not carried out, this can have the advantage of lowering costs.

[0033] The ingot is then hot-rolled and cold-rolled, giving a rolled aluminum plate. A temperature of 350 to 500°C at the start of hot rolling is appropriate. Intermediate annealing may be carried out before or after hot rolling, or even during hot rolling. The intermediate annealing conditions consist of 2 to 20 hours of heating at 280 to 600°C, and preferably 2 to 10 hours of heating at 350 to 500°C, in a batch-type annealing furnace, or of heating for up to 6 minutes at 400 to 600°C, and preferably up to 2 minutes at 450 to 550°C, in a continuous annealing furnace. Using a continuous annealing furnace to heat the rolled plate at a temperature rise rate of 10 to 200°C/sec enables a finer crystal structure to be achieved.

[0034] The aluminum plate that has been finished by the above process to a given thickness of, say, 0.1 to 0.5 mm may then be flattened with a leveling machine such as a roller leveler or a tension leveler. Flattening may be carried out after the aluminum plate has been cut into discrete sheets. However, to enhance productivity, it is preferable to carry out such flattening with the rolled aluminum plate in the state of a continuous roll. The plate may also be passed through a slitter line to cut it to a predetermined width. A thin film of oil may be provided on the aluminum plate to prevent scuffing due to rubbing between adjoining aluminum plates. Suitable use may be made of either a volatile or non-volatile oil film, as needed.

[0035] Continuous casting processes that are industrially carried out include processes which use cooling rolls, such as the twin roll process (Hunter process) and the 3C process, the twin belt process (Hazelett process), and processes which use a cooling belt or a cooling block, such as the Alusuisse Caster II process. When a continuous casting process is used, the melt is solidified at a cooling rate nf 100 to 1,000°C/sec. Continuous casting processes generally have a faster cooling rate than direct chill casting processes, and so are characterized by the ability to achieve a higher solid solubility of alloying ingredients in the aluminum matrix. Technology relating to continuous casting processes that has been disclosed by the present applicant is described in, for example, JP 3-79798 A, JP 5-201166 A, JP 5-156414 A, JP 6-262203 A, JP 6-122949 A, JP 6-210406 A and JP 6-26308 A.

[0036] When continuous casting is carried out, such as by a process involving the use of cooling rolls (e.g., the Hunter process), the melt can be directly and continuously cast as a plate having a thickness of 1 to 10 mm, thus making it possible to omit the hot rolling step. Moreover, when use is made of a process that employs cooling belts (e.g., the Hazelett process), a plate having a thickness of 10 to 50 mm can be cast. Generally, by positioning a hot-rolling roll immediately downstream of the caster, the cast plate can then be successively rolled, enabling a continuously cast and rolled plate with a thickness of 1 to 10 mm to be obtained.

[0037] These continuously cast and rolled plates are then subjected to such processes as cold rolling, intermediate annealing, flattening and slitting in the same way as described above for direct chill casting, and thereby finished to a plate thickness of 0.1 to 0.5 mm, for instance. Technology disclosed by the present applicant concerning the intermediate annealing conditions and cold rolling conditions in a continuous casting process is described in, for example, JP 6-220593 A, JP 6-210308 A, JP 7-54111 A and JP 8-92709 A.

[0038] The aluminum plate used in the present invention is well-tempered in accordance with H18 defined in JIS.

[0039] It is desirable for the aluminum plate manufactured as described above to have the following properties.

[0040] For the aluminum plate to achieve the stiffness required of a lithographic printing plate support, it should have a 0.2% proof strength of preferably at least 120 MPa. To ensure some degree of stiffness even when burning treatment has been carried out, the 0.2% proof strength following 3 to 10 minutes of heat treatment at 270°C should be preferably at least 80 MPa, and more preferably at least 100 MPa. In the case where the aluminum plate is required to have a high stiffness, use may be made of an aluminum material containing magnesium or manganese. However, because a higher stiffness lowers the ease with which the plate can be fit onto the plate cylinder of the printing press, the plate material and the amounts of minor components added thereto are suitably selected according to the intended application. Related technology disclosed by the present applicant is described in, for example, JP 7-126820 A and JP 62-140894 A.

[0041] The aluminum plate more preferably has a tensile strength of 160 ± 15 N/mm^2, a 0.2% proof strength of 140 ± 15 MPa, and an elongation as defined in JIS Z2241 and Z2201 of 1 to 10%.

[0042] Because the crystal structure at the surface of the aluminum plate may give rise to a poor surface quality when chemical graining treatment or electrochemical graining treatment is carried out, it is preferable that the crystal structure not be too coarse. The.crystal structure at the surface of the aluminum plate has a width of preferably up to 200 μm, more preferably up to 100 μm, and most preferably up to 50 μm. Moreover, the crystal structure has a length of preferably up to 5,000 μm, more preferably up to 1,000 μm, and most preferably up to 500 μm. Related technology disclosed by the present applicant is described in, for example, JP 6-218495 A, JP 7-39906 A and JP 7-124609 A.

[0043] It is preferable for the alloying ingredient distribution at the surface of the aluminum plate to be reasonably uniform because non-uniform distribution of alloying ingredients at the surface of the aluminum plate sometimes leads to a poor surface quality when chemical graining treatment or electrochemical graining treatment is carried out. Related technology disclosed by the present applicant is described in, for example, JP 6-48058 A, JP 5-301478 A and JP 7-132689 A.

[0044] The size or density of intermetallic compounds in an aluminum plate may affect chemical graining treatment or electrochemical graining treatment. Related technology disclosed by the present applicant is described in, for example, JP 7-138687 A and JP 4-254545 A.

[0045] In the present invention, the aluminum plate as described above may be used after providing recessed and protruded portions thereon in the final rolling process or the like by press rolling, transfer or another method.

[0046] In particular, it is preferable to employ a method in which a surface with a pattern of recessed and protruded portions is pressed onto the surface of the aluminum plate to transfer the pattern thereto and provide thereby the pattern of recessed and protruded portions thereon during the cold rolling for adjusting the final plate thickness or finish cold rolling for finishing the surface profile after the adjustment of the final plate thickness. More specifically, the method described in JP 6-262203 A can be advantageously used.

[0047] Use of the aluminum plate having the pattern of recessed and protruded portions transferred to its surface enhances the scumming resistance because the transferred pattern.includes recessed and protruded portions of uniform pitch and depth as compared with those formed with brushes and an abrasive. Moreover, it is possible to reduce energy consumption in subsequent alkali etching treatment and graining treatment and to facilitate control of the amount of fountain solution on a printing press. For example, the etching amount can be reduced to about 3 g/m^2 or less in a first etching treatment to be described later. In addition, the lithographic printing plate support obtained by the use of the aluminum plate having the pattern of recessed and protruded portions has an increased surface area and hence provides a better press life.

[0048] It is particularly preferable to carry out such transfer as above concurrently with the commonly performed final cold rolling. The aluminum plate is preferably rolled for transfer once to three times and the draft is preferably 3 to 8% in each rolling process.

[0049] Moreover, recessed and protruded portions are provided by the transfer preferably on both sides of the aluminum plate. In this way, the elongation percentage of the aluminum plate can be so modified as to have a similarity between the front side and the rear side of the plate and, accordingly, the aluminum plate can be improved in flatness.

[0050] Examples of the method of obtaining a roll for metal rolling which has a pattern of recessed and protruded portions provided on its surface and is used for the transfer of the recessed and protruded portions (roll being hereinafter also referred to as "transfer roll") include blasting method, electrolytic method, laser method, electrical discharge machining method and a combination thereof. Among others, a combination of blasting method and electrolytic method is preferable. Air blasting method is preferred to other blasting methods.

[0051] The air pressure employed in the air blasting method is preferably 1 to 10 kgf/cm^2 (9.81×10^4 to 9.81×10^5 Pa) and more preferably 2 to 5 kgf/cm^2 (1.96×10^5 to 4.90×10^5 Pa).

[0052] There is no particular limitation on the grit used in the air blasting method as long as alumina particles of a predetermined particle size are used. When hard alumina particles each having sharp edges are used as the grit, deep and uniform recessed and protruded portions can easily be provided on the surface of the transfer roll.

[0053] The alumina particles have an average particle size of 50 to 150 μm, preferably 60 to 130 μm and more preferably 70 to 90 μm. As having an average particle size within the above ranges, the alumina particles can impart an adequate surface roughness to the transfer roll and hence the aluminum plate having a pattern of recessed and protruded portions provided thereon using the transfer roll has an adequate surface roughness, with formed pits being large enough in number.

[0054] It is preferable to carry out two to five blasts, and more preferably two blasts, in the air blasting method. If two blasts are carried out, irregularities of the protruded portions formed by the first blast can be removed by the second blast so that deep recessed portions are hard to form locally on the surface of the aluminum plate on which recessed and protruded portions are provided using the roll for metal rolling thus obtained. In consequence, the presensitized plate obtained by the use of the aluminum plate is excellent in developability (sensitivity).

[0055] The blast angle in the air blasting method is preferably 60 to 120°, and more preferably 80 to 100°, with respect to the surface onto which air is blasted (roll surface).

[0056] It is preferable that, after the air blasting treatment, but before the subsequently described plating treatment, the transfer roll surface be polished until its average surface roughness (R_a) is reduced by 10 to 40% relative to that after the air blasting. Polishing is preferably carried out with sandpaper, a grindstone or a buff. Polishing allows the protruded portions on the surface of the transfer roll to have a uniform height so that deep recessed portions are not formed locally on the surface of the aluminum plate on which recessed and protruded portions are provided using the transfer roll. As a result, the presensitized plate obtained by the use of the aluminum plate is particularly excellent in developability (sensitivity).

[0057] The surface of the transfer roll has preferably an average surface roughness (R_a) of 0.4 to 1.0 μm and more preferably 0.6 to 0.9 μm.

[0058] The number of peaks of the transfer roll surface is preferably 1,000 to 40,000/mm^2 and more preferably 2,000 to 10,000/mm^2. If the number of peaks is too small, the water receptivity of the lithographic printing plate support and its adhesion to the image recording layer are impaired. An impaired water receptivity may cause scumming in halftone dot areas of the lithographic printing plate prepared using the support.

[0059] There is no particular limitation on the material for the transfer roll and any known material for rolls for metal rolling can be used for example.

[0060] In the present invention, it is preferable to use a roll made of steel. A steel roll fabricated by casting is particularly preferable. An exemplary composition of the preferred roll material is as follows: C: 0.07 to 6 wt%; Si: 0.2 to 1 wt%; Mn: 0.15 to 1 wt%; P: not more than 0.03 wt%; S: not more than 0.03 wt%; Cr: 2.5 to 12 wt%; Mo: 0.05 to 1.1 wt%; Cu: not more than 0.5 wt%; V: not more than 0.5 wt%; the balance: iron and inevitable impurities.

[0061] Apart from the above, examples of the preferred roll material include tool steels (SKD), high-speed tool steels (SKH), high-carbon chromium-type bearing steels (SUJ), and forged steels containing carbon, chromium, molybdenum and vanadium as alloying elements, which are generally used as a material for rolls for metal rolling. To achieve a long roll life, high-chromium alloy cast iron containing about 10 to 20 wt% of chromium may be used.

[0062] It is particularly preferable to use a roll fabricated by casting. In this case, the roll has preferably a hardness (Hs) of 80 to 100 after quenching and tempering are carried out. The tempering is preferably carried out at a low temperature.

[0063] The roll has preferably a diameter of 200 to 1,000 mm. The roll has preferably a face length of 1,000 to 4,000 mm.

[0064] The transfer roll having a pattern of recessed and protruded portions provided thereon by the air blasting method or the like is preferably subjected to a hardening treatment, such as quenching or hard chromium plating, after cleaning, which improves the wear resistance and service life of the roll.

[0065] Hard chromium plating is particularly preferable as the hardening treatment. It may be carried out by an electroplating method using a CrO_3-SO_4 bath, a CrO_3-SO_4-fluoride bath or the like that is a well-known industrial chromium plating method.

[0066] The thickness of a layer formed by the hard chromium plating is preferably 5 to 15 μm. When the thickness falls within this range, the wear resistance is adequately enhanced. The thickness of the layer formed by the hard chromium plating can be controlled through adjustment of the time for plating.

[0067] Preferably, an electrolytic treatment is performed on the transfer roll before the hard chromium plating by passing direct current through the roll as an anode in the same plating solution as to be used for the hard chromium plating at an amount of electricity of 5,000 to 50,000 C/dm^2. The treatment enables the surface of the roll to have uniform recessed and protruded portions.

[0068] The average roughness R_a of the surface of the aluminum plate is measured as follows: Two-dimensional roughness measurement is conducted using a stylus-type roughness tester (e.g., Surfcom 575 manufactured by Tokyo Seimitsu Co., Ltd.). The average roughness R_a as defined by ISO 4287 is measured five times, and the mean of the five measurements is used as the value of the average roughness.

[0069] The conditions of the two-dimensional roughness measurement are described below.

<Measurement conditions>

[0070] Cutoff value, 0.8 mm; slope correction, FLAT-ML; measurement length, 3 mm; vertical magnification, 10,000X; scan rate, 0.3 mm/sec; stylus tip diameter, 2 μm.

[0071] R_{max} and R_{sm} can be measured according to ISO 4287.

[0072] The aluminum plate used in this invention is in the form of a continuous sheet or discrete sheets. That is, it may be either an aluminum web or a cut sheet of aluminum having a size which corresponds to the presensitized plates that will be shipped as the final products.

[0073] Because scratches and other marks on the surface of the aluminum plate may become defects when the plate is fabricated into a lithographic printing plate support, it is essential to minimize the formation of such marks prior to the surface treatment operations for rendering the aluminum plate into a lithographic printing plate support. It is thus desirable for the aluminum plate to be stably packed in such a way that it will not be easily damaged during transport.

[0074] When the aluminum plate is in the form of a web, it may be packed by, for example, laying hardboard and felt on an iron pallet, placing corrugated cardboard doughnuts on either side of the product, wrapping everything with polytubing, inserting a wooden doughnut into the opening at the center of the coil, stuffing felt around the periphery of the coil, tightening steel strapping about the entire package, and labeling the exterior. In addition, polyethylene film can be used as the outer wrapping material, and needled felt and hardboard can be used as the cushioning material. Various other forms of packing exist, any of which may be used so long as the aluminum plate can be stably transported without being scratched or otherwise marked.

[0075] The aluminum plate used in the present invention has a thickness of about 0.1 to 0.6 mm, preferably 0.15 to 0.4 mm, and more preferably 0.2 to 0.3 mm. This thickness can be changed as appropriate based on such considerations as the size of the printing press, the size of the printing plate and the desires of the user.

<Surface Treatment>

[0076] According to the present invention, the aluminum plate as described above is subjected to an electrochemical graining treatment, in which alternating current is passed through the aluminum plate in an aqueous solution containing at least chloride ion and nitrate ion so that the total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2, so as to obtain a lithographic printing plate support.

[0077] In the surface treatment, various processes other than electrochemical graining treatments may be included.

[0078] Specifically, examples of a suitable surface treatment method include the method in which etching treatment in an aqueous alkali solution (hereinafter referred to as "first etching treatment"), desmutting treatment in an aqueous acidic solution (hereinafter referred to as "first desmutting treatment"), electrochemical graining treatment, etching treatment in an aqueous alkali solution (hereinafter referred to as "second etching treatment"), desmutting treatment in an aqueous acidic solution (hereinafter referred to as "second desmutting treatment"), and anodizing treatment are carried out in this order.

[0079] Another method in which sealing treatment or hydrophilizing treatment, or sealing treatment and then hydrophilizing treatment are carried out after the anodizing treatment is also preferable.

[0080] It is also possible to perform mechanical graining treatment before the first etching treatment. Mechanical graining treatment that can be used includes a wire brush graining method in which the surface of an aluminum plate is scratched with metal wire, a ball graining method in which the surface of an aluminum plate is grained with abrasive balls and an abrasive, and a brush graining method in which the surface is grained with nylon brushes and an abrasive as described in JP 6-135175 A and JP 50-40047 B.

[0081] A transfer method in which a surface with recessed and protruded portions of a transfer roll is pressed onto an aluminum plate (transfer roll method) can also be employed. Examples of applicable methods include those described in JP 55-74898 A, JP 60-36195 A and JP 60-203496 A, as well as the method described in JP 6-55871 A which is characterized in that transfer is repeated several times, and the method described in JP 6-024168 A which is characterized in that the surface is elastic.

[0082] Among these, the transfer roll method is preferable because this method is readily compatible with the speedup in the process of manufacturing a lithographic printing plate support. As described above, it is preferable in the transfer roll method to perform transfer in the cold rolling for adjusting the final plate thickness or the finish cold rolling for finishing the surface profile after the final plate thickness is adjusted.

[0083] By performing mechanical graining treatment or providing recessed and protruded portions using a transfer roll before the first etching treatment, the amount of electricity used in the electrochemical graining treatment can be reduced. In addition, such measures improve the shininess (that is to say, the ease with which the amount of fountain solution on the plate surface can be perceived during printing) of a lithographic printing plate which is prepared using the lithographic printing plate support obtained by taking the measures.

[0084] The respective surface treatment processes will be described below in detail.

<First Etching Treatment>

[0085] Alkali etching treatment is a treatment in which the surface layer of the above-described aluminum plate is dissolved by bringing the aluminum plate into contact with an alkali solution.

[0086] The purpose of the first etching treatment carried out prior to the electrochemical graining treatment is to enable the formation of uniform recesses in the electrochemical graining treatment and to remove substances such as rolling oil, contaminants and a natural oxide film from the surface of the aluminum plate (rolled aluminum).

[0087] In the first etching treatment, the surface to be subsequently subjected to the electrochemical graining treatment is treated at an etching amount, namely amount of material removed by etching, of preferably at least 0.5 g/m^2, more preferably at least 1 g/m^2, but preferably not more than 10 g/m^2, more preferably not more than 5 g/m^2. At an etching amount of 0.5 g/m^2 or more, uniform pits can be formed in the electrochemical graining treatment. At an etching amount of 10 g/m^2 or less, the amount of aqueous alkali solution used is decreased, which is economically advantageous.

[0088] On the rear side of the aluminum plate that is opposite with the surface to be subjected to the electrochemical graining treatment, the etching amount is preferably at least 5%, more preferably at least 10%, but preferably not more than 50%, more preferably not more than 30%, of the etching amount at which the surface to be subjected to the electrochemical graining treatment is treated. If the etching amount falls within the above ranges, a suitable balance can be struck between the removal effect of rolling oil on the rear side of the aluminum plate and the economical efficiency.

[0089] This is also the case with the second etching treatment to be described later.

[0090] Alkalis that may be used in the alkali solution are exemplified by caustic alkalis and alkali metal salts. Specific examples of suitable caustic alkalis include sodium hydroxide and potassium hydroxide. Specific examples of suitable alkali metal salts include alkali metal silicates such as sodium metasilicate, sodium silicate, potassium metasilicate and potassium silicate; alkali metal carbonates such as sodium carbonate and potassium carbonate; alkali metal aluminates such as sodium aluminate and potassium aluminate; alkali metal aldonates such as sodium gluconate and potassium gluconate; and alkali metal hydrogenphosphates such as sodium secondary phosphate, potassium secondary phosphate, sodium primary phosphate and potassium primary phosphate. Among others, caustic alkali solutions and solutions containing both a caustic alkali and an alkali metal aluminate are preferred on account of the high etch rate and low cost. An aqueous solution of sodium hydroxide is especially preferred.

[0091] In the first etching treatment, the alkali solution has a concentration of preferably at least 1 wt%, and more preferably at least 20 wt%, but preferably not more than 40 wt%, and more preferably not more than 35 wt%.

[0092] It is desirable for the alkali solution to contain aluminum ions. The aluminum ion concentration is preferably at least 0.5 wt%, and more preferably at least 4 wt%, but preferably not more than 10 wt%, and more preferably not more than 8 wt%. Such an alkali solution can be prepared from, for example, water, a 48 wt% solution of sodium hydroxide in water, and sodium aluminate.

[0093] In the first etching treatment, the alkali solution temperature is preferably at least 25°C, and more preferably at least 40°C, but preferably not more than 95°C, and more preferably not more than 80°C.

[0094] The treatment time in the first etching treatment is preferably at least 1 second, and more preferably at least 2 seconds, but preferably not more than 30 seconds, and more preferably not more than 10 seconds.

[0095] When the aluminum plate is continuously etched, the aluminum ion concentration in the alkali solution rises and the etching amount at which the aluminum plate is treated changes. It is thus preferable to control the etching solution composition as follows.

[0096] First, a matrix of the electrical conductivity, specific gravity and temperature or a matrix of the conductivity, ultrasonic wave propagation velocity and temperature is prepared with respect to a matrix of the sodium hydroxide concentration and the aluminum ion concentration. The solution composition is then determined based on either the conductivity, specific gravity and temperature or the conductivity, ultrasonic wave propagation velocity and temperature, and sodium hydroxide and water are added up to control target values for the solution composition. Next, the etching solution which has increased in volume with the addition of sodium hydroxide and water is allowed to overflow from a circulation tank, thereby keeping the amount of solution constant. The sodium hydroxide added may be industrial grade 40 to 60 wt% sodium hydroxide.

[0097] The conductivity meter and hydrometer used to measure electrical conductivity and specific gravity, respectively, are each preferably temperature-compensated instruments. The hydrometer is preferably a pressure differential hydrometer.

[0098] Illustrative examples of methods for bringing the aluminum plate into contact with the alkali solution include a method in which the aluminum plate is passed through a tank filled with an alkali solution, a method in which the aluminum plate is immersed in an alkali solution contained in a tank, and a method in which the surface of the aluminum plate is sprayed with an alkali solution.

[0099] The most desirable of these is a method that involves spraying the surface of the aluminum plate with an alkali solution. Specifically, in such a method, the etching solution is sprayed onto the aluminum plate from a spray line, which bears 2 to 5 mm diameter openings at a pitch of 10 to 50 mm, at a rate of 10 to 100 L/min per spray line. It is preferred that two or more spray lines are employed.

[0100] Following the completion of alkali etching treatment, it is desirable to remove the etching solution from the aluminum plate with nip rollers, subject the plate to rinsing treatment with water for 1 to 10 seconds, then remove the water with nip rollers.

[0101] Rinsing treatment is preferably carried out by rinsing with a rinsing apparatus that uses a free-falling curtain of water and then rinsing further with a spray line.

[0102] FIG. 1 is a schematic cross-sectional view of an apparatus 100 for carrying out rinsing treatment with a free-falling curtain of water. As shown in FIG. 1, the apparatus 100 that carries out rinsing with a free-falling curtain of water has a water holding tank 104 that holds water 102, a pipe 106 that feeds water to the water holding tank 104, and a flow distributor 108 that supplies a free-falling curtain of water from the water holding tank 104 to an aluminum plate 1.

[0103] In this apparatus 100, the pipe 106 feeds water 102 to the water holding tank 104. When the water 102 overflows the water holding tank 104, it is distributed by the flow distributor 108 and the free-falling curtain of water is supplied to the aluminum plate 1. A flow rate of 10 to 100 L/min is preferred when this apparatus 100 is used. The distance L between the apparatus 100 and the aluminum plate 1 over which the water 102 exists as a free-falling liquid curtain is preferably from 20 to 50 mm. Moreover, it is preferable for the aluminum plate to be inclined at an angle α to the horizontal of 30 to 80°.

[0104] By using an apparatus like that in FIG. 1 which rinses the aluminum plate with a free-falling curtain of water, the aluminum plate can be uniformly rinsed. This in turn makes it possible to enhance the uniformity of treatment carried out prior to rinsing.

[0105] A preferred example of an apparatus that carries out rinsing treatment with a free-falling curtain of water is described in JP 2003-96584 A.

[0106] Rinsing with a spray line may be carried out by the use of, for instance, a spray line having a plurality of spray tips disposed along the width of the aluminum plate, each of which discharges a fanned-out spray of water. The interval between spray tips is preferably 20 to 100 mm, and the amount of water discharged per spray tip is preferably 0.5 to 20 L/min. The use of a plurality of spray lines is preferred.

<First Desmutting Treatment>

[0107] After the first etching treatment, it is preferable to carry out acid pickling (first desmutting treatment) to remove contaminants (smut) remaining on the surface of the aluminum plate. Desmutting treatment is carried out by bringing the aluminum plate into contact with an acidic solution.

[0108] Examples of acids that may be used include nitric acid, sulfuric acid, hydrochloric acid, and chromic acid. Among these, nitric acid and sulfuric acid are preferable. For instance, an aqueous solution of sulfuric acid as the wastewater from the anodizing treatment to be described later can suitably be used.

[0109] The composition of the desmutting treatment solution may be controlled based on the electrical conductivity and temperature, or on the electrical conductivity, specific gravity and temperature, or on the electrical conductivity, ultrasonic wave propagation velocity and temperature, which parameters are corresponding to a matrix of the acidic solution concentration and the aluminum ion concentration.

[0110] In the first desmutting treatment, it is preferable to use an acidic solution containing 0.5 to 30 wt% of an acid and 0.5 to 10 wt% of aluminum ions.

[0111] The temperature of the acidic solution is preferably in the range of 25°C to 95°C.

[0112] In the first desmutting treatment, the treatment time is preferably at least 1 second, and more preferably at least 2 seconds, but preferably not more than 30 seconds, and more preferably not more than 10 seconds.

[0113] Illustrative examples of the method of bringing the aluminum plate into contact with the acidic solution include passing the aluminum plate through a tank filled with the acidic solution, immersing the aluminum plate in the acidic solution contained in a tank, and spraying the acidic solution onto the surface of the aluminum plate.

[0114] Of these, a method in which the acidic solution is sprayed onto the surface of the aluminum plate is preferred. Specifically, in such a method, the desmutting treatment solution is sprayed onto the aluminum plate from a spray line bearing 2 to 5 mm diameter openings at a pitch of 10 to 50 mm at a rate of 10 to 100 L/min per spray line. It is preferable that two or more spray lines are employed.

[0115] After desmutting treatment, it is preferable to remove the solution with nip rollers, then carry out rinsing treatment with water for 1 to 10 seconds and again remove the water with nip rollers.

[0116] Rinsing treatment is the same as the rinsing treatment following alkali etching treatment. The amount of water discharged per spray tip, however, is preferably from 1 to 20 L/min.

<Electrochemical Graining Treatment>

[0117] In the electrochemical graining treatment, alternating current is passed through the aluminum plate in an aqueous solution containing chloride ion and nitrate ion so that the total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2.

[0118] Owing to the electrochemical graining treatment of the present invention, the aluminum plate can be provided with such a surface profile by a single electrochemical graining process as including pits with an average diameter of 0.01 to 0.5 μm superimposed on recesses (pits) with an average diameter of 1 to 5 μm as shown in FIG. 2. According to the present invention, pits are formed uniformly on the plate surface after electrochemical graining treatment so as to improve the press life of a lithographic printing plate prepared and, moreover, uniform pits result in an excellent scumming resistance of the lithographic printing plate.

[0119] In the electrochemical graining treatment of the present invention, the total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2, preferably 150 to 250 C/dm^2. If the total amount of electricity when the aluminum plate serves as an anode falls within the above ranges, the aluminum plate is adequately subjected to the electrochemical graining treatment and, as a consequence, its surface is provided with asperities in which pits with an average diameter of 0.01 to 0.5 μm are uniformly superimposed on pits with an average diameter of 1 to 5 μm. In this regard, the depth of the pits with an average diameter of 0.01 to 0.5 μm is slightly decreased as compared with the case where the aluminum plate is subjected to electrochemical graining treatment by passing alternating current through the plate in an aqueous solution containing nitric acid, and then in an aqueous solution containing hydrochloric acid.

[0120] It should be noted that such a large amount of electricity as used in the method described in JP 48-28123 B causes coarse pits to be formed here and there on the aluminum plate surface, that is to say, causes the non-uniformity of pits formed on the aluminum plate surface.

[0121] The chloride ion concentration of the aqueous solution to be used as an electrolyte solution is preferably 3 to 60 g/L and more preferably 8 to 50 g/L. If the chloride ion concentration falls within the above ranges, the uniformity of pits is enhanced.

[0122] The nitrate ion concentration is preferably 0.5 to 20 g/L and more preferably 0.8 to 6 g/L. If the nitrate ion concentration falls within the ranges, the uniformity of pits is enhanced.

[0123] Chloride ions may be incorporated in the aqueous solution by using hydrochloric acid as a solution ingredient. Such chlorides as aluminum chloride, sodium chloride and ammonium chloride are also usable. Among others, aluminum chloride is preferably used. In the present invention, it is preferable to use both hydrochloric acid and a chloride, with the use of hydrochloric acid and aluminum chloride being more preferred. If hydrochloric acid is used, its concentration is preferably 3 to 30 g/L, more preferably 4 to 20 g/L, and even more preferably 5 to 18 g/L.

[0124] Nitrate ions may be incorporated in the aqueous solution by using nitric acid as a solution ingredient. Such nitrates as aluminum nitrate, sodium nitrate and ammonium nitrate are also usable. If nitric acid is used, its concentration is preferably 0.5 to 15 g/L and more preferably 1 to 10 g/L.

[0125] Incorporation of nitrate ions in the aqueous solution to be used as an electrolyte allows the pits with an average diameter of 1 to 5 μm to be formed on the aluminum plate surface and incorporation of chloride ions allows the pits with an average diameter of 0.01 to 0.5 μm to be formed on the aluminum plate surface. Therefore, the aluminum plate cannot be provided with a surface profile including pits with an average diameter of 0.01 to 0.5 μm superimposed on pits with an average diameter of 1 to 5 μm if the aqueous solution does not contain nitrate ions or chloride ions.

[0126] Preferably, the aqueous solution to be used as an electrolyte has a pH of 0.8 or less. With the solution having a pH of 0.8 or less, the uniformity of pits be even higher.

[0127] The aqueous solution to be used as an electrolyte may contain sulfuric acid.

[0128] Apart from sulfuric acid, sulfate compounds containing sulfate ion, such as aluminum sulfate, sodium sulfate and ammonium sulfate, may be incorporated in the solution.

[0129] A compound which forms a complex with copper may also be added in an amount of 1 to 200 g/L. The aqueous mixture may have dissolved therein elements which are present in the aluminum alloy, such as iron, copper, manganese, nickel, titanium, magnesium and silicon. Hypochlorous acid or hydrogen peroxide may be added in an amount of 1 to 100 g/L.

[0130] The aqueous solution preferably has an aluminum ion concentration of at least 2 g/L, more preferably 3 to 30 g/L and even more preferably 3 to 20 g/L, especially 4 to 18 g/L. If the aluminum ion concentration falls within the above ranges, the uniformity of pits is enhanced. In addition, excess replenishment of the aqueous solution can be avoided.

[0131] Aluminum ions may be incorporated in the aqueous solution by dissolving an aluminum salt in the solution. Examples of a usable aluminum salt include aluminum chloride, aluminum nitrate and aluminum sulfate, among which aluminum chloride or aluminum nitrate containing chloride ion or nitrate ion to be incorporated in the aqueous solution is more suitable for use because of making the pit shape better.

[0132] It is preferable to perform concentration control of each component of an electrolyte solution using a concentration measuring method such as multi-component concentration measurement in combination with feedforward control and feedback control. This makes it possible to accurately control the concentration of the electrolyte solution.

[0133] Examples of the multi-component concentration measuring method include a method in which the concentration is measured using the ultrasonic wave propagation velocity in the electrolyte solution and the electrical conductivity (electrical conductance) of the electrolyte solution, neutralization titration, capillary electrophoretic analysis, capillary isotachophoretic analysis, and ion chromatography.

[0134] Depending on the type of a detector used, methods for ion chromatography are classified into those using an ion chromatograph for absorbance detection, those using a non-suppressor type ion chromatograph for electrical conductivity detection, those using a suppressor type ion chromatograph, and so forth. Among others, the ion chromatography using a suppressor type ion chromatograph is preferable because the measurement stability is secured.

[0135] The current density employed in the electrochemical graining treatment is preferably 10 to 300 A/dm^2, more preferably 15 to 200 A/dm^2, and even more preferably 20 to 125 A/dm^2 as a peak current value. A current density of 10 A/dm^2 or more increases the productivity. If the current density is 300 A/dm^2 or less, the voltage is not elevated and the power supply capacity can be moderate, power supply costs being thus suppressed.

[0136] The electrochemical graining treatment may be carried out in accordance with, for example, the electrochemical graining processes (electrolytic graining processes) described in JP 48-28123 B and GB 896,563.

[0137] Various electrolytic cells and power supplies have been proposed for use in electrolytic treatment. For example, use may be made of those described in US 4,203,637, JP 56-123400 A, JP 57-59770 A, JP 53-12738 A, JP 53-32821

A, JP 53-32822 A, JP 53-32823 A, JP 55-122896 A, JP 55-132884 A, JP 62-127500 A, JP 1-52100 A, JP 1-52098 A, JP 60-67700 A, JP 1-230800 A, JP 3-257199 A, JP 52-58602 A, JP 52-152302 A, JP 53-12738 A, JP 53-12739 A, JP 53-32821 A, JP 53-32822 A, JP 53-32833 A, JP 53-32824 A, JP 53-32825 A, JP 54-85802 A, JP 55-122896 A, JP 55-132884 A, JP 48-28123 B, JP 51-7081 B, JP 52-133838 A, JP 52-133840 A, JP 52-133844 A, JP 52-133845 A, JP 53-149135 A and JP 54-146234 A.

[0138] By adding and using a compound capable of forming a complex with copper, uniform graining may be carried out even on an aluminum plate having a high copper content. Examples of the compound capable of forming a complex with copper include ammonia; amines obtained by substituting the hydrogen atom on ammonia with a hydrocarbon group (of an aliphatic, aromatic, or other nature), such as methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine, cyclohexylamine, triethanolamine, triisopropanolamine and ethylenediamine tetraacetate (EDTA); and metal carbonates such as sodium carbonate, potassium carbonate and potassium hydrogencarbonate. Additional compounds suitable for this purpose include ammonium salts such as ammonium nitrate, ammonium chloride, ammonium sulfate, ammonium phosphate and ammonium carbonate.

[0139] The temperature of the aqueous mixture is preferably at least 20°C, more preferably at least 25°C and even more preferably at least 30°C, but is preferably not more than 60°C, more preferably not more than 50°C and even more preferably not more than 40°C. If the temperature is at least 20°C, the cost required for operating a refrigerator for cooling is not increased and the amount of ground water used for cooling can be suppressed. If the temperature is not more than 60°C, the corrosion resistance of the facilities can be easily ensured.

[0140] No particular limitation is imposed on the alternating current waveform used in the electrochemical graining treatment. For example, a sinusoidal, square, trapezoidal or triangular waveform may be used.

[0141] The frequency of the alternating current is preferably 10 to 200 Hz, more preferably 20 to 150 Hz and even more preferably 50 to 60 Hz. If the frequency is 10 Hz or more, large pits of a facetted (squarish) shape are hard to form, resulting in a more excellent scumming resistance. At a frequency of 200 Hz or less, the electrolytic current is not susceptible to inductance components of a circuit through which the current is passed and the production of a power supply of high capacity is thus facilitated.

[0142] "Trapezoidal waveform" refers herein to such a waveform as shown in FIG. 3. In the trapezoidal waveform, the time TP in which the current value changes from zero to a peak is preferably 0.3 to 2.0 msec and more preferably 0.5 to 0.8 msec. If the time is at least 0.3 msec, the cost required for the production of a power supply is decreased. If the time is not more than 2 msec, a higher uniformity of pits is attained. In the case of triangular waveform, the current rise time can be set as appropriate.

[0143] As the power supply equipment, a power supply using a commercial alternating current or an inverter-controlled power supply can be used, for example. Among others, an inverter-controlled power supply using an insulated gate bipolar transistor (IGBT) is preferable because any waveform can be generated under the pulse width modulation (PWM) control in the equipment. Moreover, such a power supply is excellent in follow-up performance when the current value (current density in the aluminum plate) is kept constant by changing the voltage in accordance with the width and thickness of the aluminum plate, the variation in concentration of the individual components in the electrolyte solution, and so forth.

[0144] FIG. 4 is a schematic view of a radial electrolytic cell such as may be employed to carry out the electrochemical graining treatment using alternating current in the method of manufacturing a lithographic printing plate support according to the present invention.

[0145] One or more AC power supplies may be connected to the electrolytic cell. To control the anode/cathode current ratio of the alternating current applied to the aluminum plate opposite the main electrodes and thereby carry out uniform graining and to dissolve carbon from the main electrodes, it is advantageous to provide an auxiliary anode and divert some of the alternating current, as shown in FIG. 4. FIG. 4 shows an aluminum plate 11, a radial drum roller 12, main electrodes 13a and 13b, an electrolytic treatment solution 14, a solution feed inlet 15, a slit 16, a solution channel 17, an auxiliary anode 18, thyristors 19a and 19b, an AC power supply 20, a main electrolytic cell 40 and an auxiliary anode cell 50. By using a rectifying or switching device to divert some of the current as direct current to the auxiliary anode provided in the separate cell from that containing the two main electrodes, it is possible to control the ratio between the current value when the aluminum plate opposite the main electrodes serves as an anode and the current value when the aluminum plate serves as a cathode. The current ratio (ratio between the total amount of electricity when the aluminum plate serves as an anode and the total amount of electricity when the aluminum plate serves as an cathode) is preferably 0.9 to 3 and more preferably 0.9 to 1.0.

[0146] Any known electrolytic cell employed for surface treatment, including vertical, flat and radial type electrolytic cells, may be used in the method of manufacturing a lithographic printing plate support of the present invention. Radial-type electrolytic cells such as described in JP 5-195300 A are especially preferred. The electrolyte solution passes through the electrolytic cell either parallel or counter to the direction in which the aluminum web advances.

[0147] The electrolytic cell may be divided into sections. In that case, electrolysis may be carried out in the respective sections under the same or different conditions.

[0148] Following completion of the electrochemical graining treatment, it is desirable to remove the solution from the aluminum plate with nip rollers, rinse the plate with water for 1 to 10 seconds, then remove the water with nip rollers.

[0149] Rinsing treatment is preferably carried out using a spray line. The spray line used in rinsing treatment is typically one having a plurality of spray tips disposed along the width of the aluminum plate, each of which discharges a fanned-out spray of water. The interval between the spray tips is preferably 20 to 100 mm, and the amount of water discharged per spray tip is preferably 1 to 20 L/min. The use of a plurality of spray lines is preferred.

<Second Etching Treatment>

[0150] Preferably, a second etching treatment is carried out after the electrochemical graining treatment. The purpose of the second etching treatment is to dissolve smut that arises in the electrochemical graining treatment and to dissolve the edges of the pits formed by the electrochemical graining treatment. The present step dissolves the edges of the large pits formed by the electrochemical graining treatment, smoothing the surface and discouraging ink from catching on such edges. As a result, presensitized plates of excellent scumming resistance can be obtained.

[0151] The second etching treatment is basically the same as the first etching treatment except the following points: The aluminum ion concentration in the alkali solution is preferably 0.1 to 10 wt%; it is more preferable to use a 20 to 40 wt% alkali solution containing 4 to 8 wt% of aluminum ions or a 4 to 6 wt% alkali solution containing 0.3 to 0.7 wt% of aluminum ions; and the temperature of the solution is more preferably 30 to 80°C.

[0152] The etching amount is preferably at least 0.01 g/m^2, more preferably at least 0.05 g/m^2 and even more preferably at least 0.1 g/m^2, but preferably not more than 10 g/m^2, more preferably not more than 3 g/m^2 and even more preferably not more than 0.3 g/m^2.

<Second Desmutting Treatment>

[0153] After the second etching treatment has been carried out, it is preferable to carry out acid pickling (second desmutting treatment) to remove contaminants (smut) remaining on the surface of the aluminum plate. The second desmutting treatment can basically be carried out in the same way as the first desmutting treatment.

[0154] If the desmutting treatment solution used in the second desmutting treatment is the same type of solution as the electrolyte solution used in the anodizing treatment subsequently carried out, removal of the solution with nip rollers and rinsing may not be performed on the plate after the desmutting treatment.

[0155] The second desmutting treatment is preferably carried out in an electrolytic cell of an anodizing apparatus used in the anodizing treatment to be described later, in which cell the aluminum plate is to be subjected to cathodic reaction. This configuration eliminates the necessity for providing an independent desmutting treatment cell for the second desmutting treatment, which can lead to equipment cost reduction.

<Anodizing Treatment>

[0156] It is preferable that the aluminum plate treated as described above is further subjected to anodizing treatment. Anodizing treatment can be carried out by any suitable method used in the field to which the present invention pertains. More specifically, an anodized layer can be formed on the aluminum plate surface by, for example, passing a current through the aluminum plate as an anode in a solution having a sulfuric acid concentration of 50 to 300 g/L and an aluminum concentration of up to 5 wt%. The solution used for anodizing treatment may include sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid, amidosulfonic acid or the like alone or in combination.

[0157] In this connection, components ordinarily present in at least the aluminum plate, electrodes, tap water, ground water and the like are acceptable in the electrolyte solution. In addition, secondary and tertiary components may be added. Examples of the "secondary and tertiary components" include ions of such a metal as sodium, potassium, magnesium, lithium, calcium, titanium, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc; cations such as ammonium ions; and anions such as nitrate ions, carbonate ions, chloride ions, phosphate ions, fluoride ions, sulfite ions, titanate ions, silicate ions and borate ions. These may be present in a concentration of about 0 to 10,000 ppm.

[0158] The anodizing treatment conditions vary empirically according to the electrolyte solution used, although it is generally suitable for the electrolyte solution to have a concentration of 1 to 80 wt% and a temperature of 5 to 70°C, and for the current density to be 0.5 to 60 A/dm^2, the voltage to be 1 to 100 V, and the electrolysis time to be 15 seconds to 50 minutes. These conditions may be adjusted to obtain the desired anodized layer weight.

[0159] Methods that may be used to carry out anodizing treatment include those described in JP 54-81133 A, JP 57-47894 A, JP 57-51289 A, JP 57-51290 A, JP 57-54300 A, JP 57-136596 A, JP 58-107498 A, JP 60-200256 A, JP 62-136596 A, JP 63-176494 A, JP 4-176897 A, JP 4-280997 A, JP 6-207299 A, JP 5-24377 A, JP 5-32083 A, JP 5-125597 A and JP 5-195291 A.

[0160] Among others, it is preferable to use a sulfuric acid solution as the electrolyte solution, as described in JP 54-12853 A and JP 48-45303 A. The solution has a sulfuric acid concentration of preferably 10 to 300 g/L (1 to 30 wt%), and more preferably 50 to 200 g/L (5 to 20 wt%), and an aluminum ion concentration of preferably 1 Lu 25 g/L (0.1 to 2.5 wt%), and more preferably 2 to 10 g/L (0.2 to 1 wt%). Such an electrolyte solution can be prepared by, for instance, adding aluminum sulfate to a dilute sulfuric acid having a sulfuric acid concentration of 50 to 200 g/L.

[0161] Control of the electrolyte solution composition is preferably carried out using a method similar to that employed in the nitric acid electrolysis as described before. That is, the composition may be controlled based on the electrical conductivity, specific gravity and temperature, or on the electrical conductivity, ultrasonic wave propagation velocity and temperature, which parameters are corresponding to a matrix of the sulfuric acid concentration and the aluminum ion concentration.

[0162] The electrolyte solution has a temperature of preferably 25 to 55°C, and more preferably 30 to 50°C.

[0163] When anodizing treatment is carried out in an electrolyte solution containing sulfuric acid, direct current or alternating current may be applied across the aluminum plate and the counter electrode.

[0164] When a direct current is applied to the aluminum plate, the current density is preferably 1 to 60 A/dm^2, and more preferably 5 to 40 A/dm^2.

[0165] To keep burnt deposits (areas of the anodized layer which are thicker than surrounding areas) from arising on portions of the aluminum plate due to the concentration of current when anodizing treatment is carried out as a continuous process, it is preferable to apply current at a low density of 5 to 10 A/dm^2 at the start of anodizing treatment and to increase the current density to 30 to 50 A/dm^2 or more as anodizing treatment proceeds.

[0166] Specifically, it is preferable for current from the DC power supplies to be allocated such that current from downstream DC power supplies is equal to or greater than current from upstream DC power supplies. Current allocation in this way will discourage the formation of burnt deposits, enabling high-speed anodization to be carried out.

[0167] When anodizing treatment is carried out as a continuous process, this is preferably done using a system that supplies power to the aluminum plate through the electrolyte solution.

[0168] By carrying out anodizing treatment under such conditions, a porous film with numerous micropores can be obtained. The film generally has an average pore diameter of about 5 to 50 nm and an average pore density of about 300 to 800 pores/μm^2.

[0169] The weight of the anodized layer is preferably 1 to 5 g/m^2. At a weight of 1 g/m^2 or more, scratches are not readily formed on the plate. A weight of not more than 5 g/m^2 does not require a large amount of electrical power for the formation of the layer, which is economically advantageous. An anodized layer weight of 1.5 to 4 g/m^2 is more preferred. It is also desirable for anodizing treatment to be carried out in such a way that the difference in the anodized layer weight between the center of the aluminum plate and the areas near the edges is not more than 1 g/m^2.

[0170] The weight of the anodized layer on the rear side of the aluminum plate that is opposite with the surface having been subjected to the electrochemical graining treatment is preferably 0.1 to 1 g/m^2. At a weight of 0.1 g/m^2 or more, scratches are not readily formed on the rear surface and hence when the presensitized plates are stacked on top of each other, scuffing of the image recording layer brought into contact with the rear surface is prevented. A weight of not more than 1 g/m^2 is economically advantageous.

[0171] Examples of electrolyzing apparatuses that may be used in anodizing treatment include those described in JP 48-26638 A, JP 47-18739 A, JP 58-24517 B and JP 2001-11698 A.

[0172] Among others, an apparatus like that shown in FIG. 5 is preferred. FIG. 5 is a schematic view showing an exemplary apparatus for anodizing the surface of an aluminum plate.

[0173] In an anodizing apparatus 410 shown in FIG. 5, to apply a current to an aluminum plate 416 through an electrolyte solution, a power supplying cell 412 is disposed upstream in the direction of advance of the aluminum plate 416 and an anodizing treatment tank 414 downstream. The aluminum plate 416 is moved by path rollers 422 and 428 in the direction indicated by the arrows in FIG. 5. The power supplying cell 412 through which the aluminum plate 416 first passes is provided with anodes 420 which are connected to the positive poles of a DC power supply 434, and the aluminum plate 416 serves as the cathode in the cell. Hence, a cathodic reaction arises at the aluminum plate 416.

[0174] The anodizing treatment tank 414 through which the aluminum plate 416 next passes is provided with a cathode 430 which is connected to the negative pole of the DC power supply 434, and the aluminum plate 416 serves as the anode in the tank. Hence, an anodic reaction arises at the aluminum plate 416, and an anodized layer is formed on the surface of the aluminum plate 416.

[0175] The aluminum plate 416 is at a distance of preferably 50 to 200 mm from the cathode 430. The cathode 430 is made of aluminum. To facilitate the venting of hydrogen gas generated by the anodic reaction from the system, it is preferable for the cathode 430 to be divided into a plurality of sections in the direction of advance of the aluminum plate 416 rather than to be a single electrode having a broad surface area.

[0176] As shown in FIG. 5, it is advantageous to provide, between the power supplying cell 412 and the anodizing treatment tank 414, an intermediate tank 413 that does not hold the electrolyte solution. By providing the intermediate tank 413, the current can be kept from passing directly from the anode 420 to the cathode 430 and bypassing the aluminum plate 416. It is preferable to minimize the bypass current by providing nip rollers 424 in the intermediate tank 413 to remove the solution from the aluminum plate 416. The electrolyte solution removed by the nip rollers 424 is discharged outside the anodizing apparatus 410 through a discharge outlet 112.

[0177] To lower the voltage loss, an electrolyte solution 418 contained in the power supplying cell 412 is set at a higher temperature and/or concentration than an electrolyte solution 426 contained in the anodizing treatment tank 414. Moreover, the composition, temperature and other characteristics of the electrolyte solutions 418 and 426 are set based on such considerations as the anodized layer forming efficiency, the shapes of micropores in the anodized layer, the hardness of the anodized layer, the voltage, and the cost of the electrolyte solution.

[0178] The power supplying cell 412 and the anodizing treatment tank 414 are supplied with electrolyte solutions injected by solution feed nozzles 436 and 438. To ensure that the distribution of electrolyte solution remains uniform and thereby prevent the localized concentration of current on the aluminum plate 416 in the anodizing treatment tank 414, the solution feed nozzles 436 and 438 have a construction in which slits are provided to keep the flow of injected liquid constant in the width direction.

[0179] In the anodizing treatment tank 414, a shield 440 is provided on the opposite side of the aluminum plate 416 from the cathode 430 to check the flow of current to the opposite surface of the aluminum plate 416 with the surface on which an anodized layer is to be formed. The interval between the aluminum plate 416 and the shield 440 is preferably 5 to 30 mm. It is preferable to use a plurality of DC power supplies as the DC power supply 434, with their positive poles being connected in common, thereby enabling control of the current distribution within the anodizing treatment tank 414.

[0180] When the anodizing treatment is carried out, one anodizing apparatus 410 may be used but the anodizing treatment is preferably carried out as a continuous process by arranging two to five anodizing apparatuses 410 in series in the direction in which the aluminum plate advances. This is effective in high speed processing and reduction of electric power used.

<Sealing Treatment>

[0181] Sealing treatment may be carried out as required to seal micropores in the anodized layer. Such treatment can enhance the developability (sensitivity) of the presensitized plate.

[0182] Anodized layers are known to be porous films having micropores which extend in a direction substantially perpendicular to the surface of the film. In the present invention, it is advantageous to carry out sealing treatment to a high sealing ratio following the anodizing treatment. The sealing ratio is preferably at least 50%, more preferably at least 70%, and even more preferably at least 90%. "Sealing ratio," as used herein, is defined as follows.

$$\text{Sealing ratio} = [(\text{surface area before sealing}) - (\text{surface area after sealing})]/(\text{surface area before sealing}) \times 100\%$$

[0183] The surface area can be measured using a simple BET-type surface area analyzer, such as Quantasorb (Yuasa Ionics Inc.).

[0184] Sealing may be carried out using any known method without particular limitation. Illustrative examples of sealing methods that may be used include hot water treatment, boiling water treatment, steam treatment, dichromate treatment, nitrite treatment, ammonium acetate treatment, electrodeposition sealing treatment, hexafluorozirconic acid treatment like that described in JP 36-22063 B, treatment with an aqueous solution containing a phosphate and an inorganic fluorine compound as described in JP 9-244227 A, treatment with a sugar-containing aqueous solution as described in JP 9-134002 A, treatment with a titanium and fluorine-containing aqueous solution as described in JP 2000-81704 A and JP 2000-89466 A, and alkali metal silicate treatment like that described in US 3,181,461.

[0185] One preferred type of sealing treatment is alkali metal silicate treatment. This can be carried out using a pH 10 to 13 aqueous solution of an alkali metal silicate at 25°C that does not undergo solution gelation or dissolve the anodized layer, and by suitably selecting the treatment conditions, such as the alkali metal silicate concentration, the treatment temperature and the treatment time. Preferred alkali metal silicates include sodium silicate, potassium silicate and lithium silicate. Sodium hydroxide, potassium hydroxide, lithium hydroxide or the like may be incorporated in the aqueous solution of alkali metal silicate in order to increase the pH thereof.

[0186] If necessary, an alkaline earth metal salt and/or a Group 4 (Group IVA) metal salt may also be included in the aqueous alkali metal silicate solution. Examples of suitable alkaline earth metal salts include the following water-soluble salts: nitrates such as calcium nitrate, strontium nitrate, magnesium nitrate and barium nitrate; and also sulfates, hydrochlorides, phosphates, acetates, oxalates, and borates of alkaline earth metals. Exemplary Group 4 (Group IVA) metal salts include titanium tetrachloride, titanium trichloride, titanium potassium fluoride, titanium potassium oxalate, titanium sulfate, titanium tetraiodide, zirconyl chloride, zirconium dioxide and zirconium tetrachloride. These alkaline earth metal salts and Group 4 (Group IVA) metal salts may be used singly or in combinations of two or more thereof.

[0187] The concentration of the aqueous alkali metal silicate solution is preferably 0.01 to 10 wt%, and more preferably 0.05 to 5.0 wt%.

[0188] Another preferred type of sealing treatment is hexafluorozirconic acid treatment. Such treatment is carried out using a hexafluorozirconate such as sodium hexafluorozirconate and potassium hexafluorozirconate. It is particularly preferable to use sodium hexafluorozirconate. This treatment provides the presensitized plate with excellent developability (sensitivity). The hexafluorozirconate solution used in this treatment has a concentration of preferably 0.01 to 2 wt%, and more preferably 0.1 to 0.3 wt%.

[0189] It is desirable for the hexafluorozirconato solution to contain sodium dihydrogenphosphate in a concentration of preferably 0.01 to 3 wt%, and more preferably 0.1 to 0.3 wt%.

[0190] The hexafluorozirconate solution may contain aluminum ions. In this case, the hexafluorozirconate solution has preferably an aluminum ion concentration of 1 to 500 mg/L.

[0191] The sealing treatment temperature is preferably 20 to 90°C, and more preferably 50 to 80°C.

[0192] The sealing treatment time (period of immersion in the solution) is preferably 1 to 20 seconds, and more preferably 5 to 15 seconds.

[0193] If necessary, sealing treatment may be followed by surface treatment such as the above-described alkali metal silicate treatment or treatment in which the aluminum plate is immersed in or coated with a solution containing polyvinylphosphonic acid, polyacrylic acid, a polymer or copolymer having pendant groups such as sulfo groups, or any of the organic compounds, or salts thereof, as described in JP 11-231509 A which has an amino group and a phosphine group, phosphone group or phosphoric acid group.

[0194] Following sealing treatment, it is desirable to carry out the hydrophilizing treatment described below.

<Hydrophilizing Treatment>

[0195] Hydrophilizing treatment may be carried out after anodizing treatment or sealing treatment. Illustrative examples of suitable hydrophilizing treatments include the potassium hexafluorozirconate treatment described in US 2,946,638, the phosphomolybdate treatment described in US 3,201,247, the alkyl titanate treatment described in GB 1,108,559, the polyacrylic acid treatment described in DE 1,091,433, the polyvinylphosphonic acid treatments described in DE 1,134,093 and GB 1,230,447, the phosphonic acid treatment described in JP 44-6409 B, the phytic acid treatment described in US 3,307,951, the treatments involving the divalent metal salt of a lipophilic organic polymeric compound described in JP 58-16893 A and JP 58-18291 A, a treatment like that described in US 3,860,426 in which an undercoat of a hydrophilic cellulose (e.g., carboxymethyl cellulose) containing a water-soluble metal salt (e.g., zinc acetate) is provided, and the treatment as described in JP 59-101651 A in which a sulfo group-bearing water-soluble polymer is undercoated.

[0196] Additional examples of suitable hydrophilizing treatments include undercoating treatment using the phosphates described in JP 62-019494 A, the water-soluble epoxy compounds described in JP 62-033692 A, the phosphoric acid-modified starches described in JP 62-097892 A, the diamine compounds described in JP 63-056498 A, the inorganic or organic salts of amino acids described in JP 63-130391 A, the carboxy or hydroxy group-bearing organic phosphonic acids described in JP 63-145092 A, the amino group and phosphonic acid group-bearing compounds described in JP 63-165183 A, the specific carboxylic acid derivatives described in JP 2-316290 A, the phosphate esters described in JP 3-215095 A, the compounds having one amino group and one phosphorus oxoacid group described in JP 3-261592 A, the aliphatic or aromatic phosphonic acids (e.g., phenylphosphonic acid) described in JP 5-246171 A, the sulfur atom-bearing compounds (e.g., thiosalicylic acid) described in JP 1-307745 A, and the phosphorus oxoacid group-bearing compounds described in JP 4-282637 A.

[0197] Coloration with an acid dye as described in JP 60-64352 A may also be carried out.

[0198] It is preferable to carry out hydrophilizing treatment by a method in which the aluminum plate is immersed in an aqueous solution of an alkali metal silicate such as sodium silicate or potassium silicate, or is coated with a hydrophilic vinyl polymer or some other hydrophilic compound so as to form a hydrophilic undercoat.

[0199] Hydrophilizing treatment with an aqueous solution of an alkali metal silicate such as sodium silicate or potassium silicate can be carried out according to the processes and procedures described in US 2,714,066 and US 3,181,461.

[0200] Illustrative examples of suitable alkali metal silicates include sodium silicate, potassium silicate and lithium silicate. Suitable amounts of sodium hydroxide, potassium hydroxide, lithium hydroxide or the like may be included in the aqueous alkali metal silicate solution.

[0201] An alkaline earth metal salt or a Group 4 (Group IVA) metal salt may also be included in the aqueous alkali metal silicate solution. Examples of suitable alkaline earth metal salts include nitrates such as calcium nitrate, strontium nitrate, magnesium nitrate and barium nitrate; and also sulfates, hydrochlorides, phosphates, acetates, oxalates, and borates. Exemplary Group 4 (Group IVA) metal salts include titanium tetrachloride, titanium trichloride, titanium potassium fluoride, titanium potassium oxalate, titanium sulfate, titanium tetraiodide, zirconyl chloride, zirconium dioxide and zirconium tetrachloride. These alkaline earth metal salts and Group 4 (Group IVA) metal salts may be used singly or in combinations of two or more thereof.

[0202] The amount of silicon adsorbed as a result of alkali metal silicate treatment can be measured with a fluorescent x-ray analyzer, and is preferably about 1.0 to 15.0 mg/m^2.

[0203] This alkali metal silicate treatment has the effect of enhancing the resistance at the surface of the lithographic printing plate support to dissolution by the alkaline developer, suppressing the leaching of aluminum ingredients into the developer, and reducing the generation of development scum due to developer fatigue.

[0204] Hydrophilizing treatment involving the formation of a hydrophilic undercoat can also be carried out in accordance with the conditions and procedures described in JP 59-101651 A and JP 60-149491 A.

[0205] Hydrophilic vinyl polymers that may be used in such a method include copolymers of a sulfo group-bearing vinyl polymerizable compound such as polyvinylsulfonic acid or sulfo group-bearing p-styrenesulfonic acid with a conventional vinyl polymerizable compound such as an alkyl (meth)acrylate.

Examples of hydrophilic compounds that may be used in this method include compounds having at least one group selected from among -NH$_2$ groups, -COOH groups and sulfo groups.

<Drying>

[0206] After the lithographic printing plate support has been obtained as described above, it is advantageous to dry the surface of the support before providing an image recording layer thereon. Drying is preferably carried out after the support has been rinsed with water and the water removed with nip rollers following the final surface treatment.

[0207] The drying temperature is preferably at least 70°C, and more preferably at least 80°C, but preferably not more than 110°C, and more preferably not more than 100°C.

[0208] The drying time is preferably at least 1 second, and more preferably at least 2 seconds, but preferably not more than 20 seconds, and more preferably not more than 15 seconds.

[Presensitized Plate]

[0209] The lithographic printing plate support according to the present invention can be formed into a presensitized plate of the present invention by providing an image recording layer thereon. A photosensitive composition is used in the image recording layer.

[0210] Preferred examples of photosensitive compositions that may be used in the present invention include thermal positive-type photosensitive compositions containing an alkali-soluble polymeric compound and a photothermal conversion substance (such compositions and the image recording layers obtained using these compositions are referred to below as "thermal positive-type" compositions and image recording layers), thermal negative-type photosensitive compositions containing a curable compound and a photothermal conversion substance (these compositions and the image recording layers obtained therefrom are similarly referred to below as "thermal negative-type" compositions and image recording layers), photopolymerizable photosensitive compositions (referred to below as "photopolymer-type" compositions), negative-type photosensitive compositions containing a diazo resin or a photo-crosslinkable resin (referred to below as "conventional negative-type" compositions), positive-type photosensitive compositions containing a quinonediazide compound (referred to below as "conventional positive-type" compositions), and photosensitive compositions that do not require a special development step (referred to below as "non-treatment type" compositions). The thermal positive-type, thermal negative-type and non-treatment type compositions are particularly preferred. These preferred photosensitive compositions are described below.

<Thermal Positive-Type Photosensitive Compositions>

<Photosensitive layer>

[0211] Thermal positive-type photosensitive compositions contain an alkali-soluble polymeric compound and a photothermal conversion substance. In a thermal positive-type image recording layer, the photothermal conversion substance converts light energy such as from an infrared laser into heat, which efficiently eliminates interactions that lower the alkali solubility of the alkali-soluble polymeric compound.

[0212] The alkali-soluble polymeric compound may be, for example, a resin having an acidic group on the molecule, or a mixture of two or more such resins. Resins having an acidic group, such as a phenolic hydroxy group, a sulfonamide group (-SO$_2$NH-R, wherein R is a hydrocarbon group) or an active imino group (-SO$_2$NHCOR, -SO$_2$NHSO$_2$R or -CONHSO$_2$R, wherein R is as defined above), are especially preferred on account of their solubility in alkaline developers.

[0213] For an excellent image formability with exposure to light from an infrared laser, for example, resins having phenolic hydroxy groups are especially desirable. Preferred examples of such resins include novolak resins such as phenol-formaldehyde resins, m-cresol-formaldehyde resins, p-cresol-formaldehyde resins, cresol-formaldehyde resins in which the cresol is a mixture of m-cresol and p-cresol, and phenol/cresol mixture-formaldehyde resins (phenol-cresol-formaldehyde co-condensation resins) in which the cresol is m-cresol, p-cresol or a mixture of m- and p-cresol.

[0214] Additional preferred examples include the polymeric compounds described in JP 2001-305722 A (especially paragraphs [0023] to [0042]), the polymeric compounds having recurring units of general formula (1) described in JP 2001-215693 A, and the polymeric compounds described in JP 2002-311570 A (especially paragraph [0107]).

[0215] To provide a good recording sensitivity, the photothermal conversion substance is preferably a pigment or dye that absorbs light in the infrared wavelength range of 700 to 1200 nm. Illustrative examples of suitable dyes include azo dyes, metal complex azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium salts and metal-thiolate complexes (e.g., nickel-thiolate complexes). Of these, cyanine dyes are preferred. The cyanine dyes of general formula (I) described in JP 2001-305722 A are especially preferred.

[0216] A dissolution inhibitor may be included in thermal positive-type photosensitive compositions. Preferred examples of dissolution inhibitors include those described in paragraphs [0053] to [0055] of JP 2001-305722 A.

[0217] The thermal positive-type photosensitive compositions preferably also include, as additives, sensitivity regulators, print-out agents for obtaining a visible image immediately after heating from light exposure, compounds such as dyes as image colorants, and surfactants for enhancing coatability and treatment stability. Compounds such as described in paragraphs [0056] to [0060] of JP 2001-305722 A are preferred additives.

[0218] Use of the photosensitive compositions described in detail in JP 2001-305722 A is desirable because of the above preferred components and additional advantages.

[0219] The thermal positive-type image recording layer is not limited to a single layer, but may have a two-layer construction.

[0220] Preferred examples of image recording layers with a two-layer construction (also referred to as "multilayer-type image recording layers") include those comprising a bottom layer ("layer A") of excellent press life and solvent resistance which is provided on the side close to the support and a layer ("layer B") having an excellent positive-image formability which is provided on layer A. This type of image recording layer has a high sensitivity and can provide a broad development latitude. Layer B generally contains a photothermal conversion substance. Preferred examples of the photothermal conversion substance include the dyes mentioned above.

[0221] Preferred examples of resins that may be used in layer A include polymers that contain as a copolymerizable component a monomer having a sulfonamide group, an active imino group or a phenolic hydroxy group; such polymers have an excellent press life and solvent resistance. Preferred examples of resins that may be used in layer B include phenolic hydroxy group-bearing resins which are soluble in aqueous alkali solutions.

[0222] In addition to the above resins, various additives may be included, if necessary, in the compositions used to form layers A and B. For example, suitable use can be made of the additives described in paragraphs [0062] to [0085] of JP 2002-323769 A. The additives described in paragraphs [0053] to [0060] of JP 2001-305722 A as above are also suitable for use.

[0223] The components and proportions thereof in each of layers A and B are preferably selected as described in JP 11-218914 A.

<Intermediate layer>

[0224] It is advantageous to provide an intermediate layer between the thermal positive-type image recording layer and the support. Preferred examples of ingredients that may be used in the intermediate layer include the various organic compounds described in paragraph [0068] of JP 2001-305722 A.

<Others>

[0225] The methods described in detail in JP 2001-305722 A may be used to form a thermal positive-type image recording layer and to make a printing plate having such a layer.

<Thermal Negative-Type Photosensitive Compositions>

[0226] Thermal negative-type photosensitive compositions contain a curable compound and a photothermal conversion substance. A thermal negative-type image recording layer is a negative-type photosensitive layer in which areas irradiated with light such as from an infrared laser cure to form image areas.

<Polymerizable layer>

[0227] An example of a preferred thermal negative-type image recording layer is a polymerizable image recording layer (polymerizable layer). The polymerizable layer contains a photothermal conversion substance, a radical generator, a radical-polymerizable compound which is a curable compound, and a binder polymer. In the polymerizable layer, the photothermal conversion substance converts absorbed infrared light into heat, and the heat decomposes the radical generator, thereby generating radicals. The radicals then trigger the chain polymerization and curing of the radical-polymerizable compound.

[0228] Illustrative examples of the photothermal conversion substance include photothermal conversion substances that may be used in the above-described thermal positive-type photosensitive compositions. Specific examples of cyanine dyes, which are especially preferred, include those described in paragraphs [0017] to [0019] of JP 2001-133969 A.

[0229] Preferred radical generators include onium salts. The onium salts described in paragraphs [0030] to [0033] of JP 2001-133969 A are especially preferred.

[0230] Exemplary radical-polymerizable compounds include compounds having one, and preferably two or more, terminal ethylenically unsaturated bonds.

[0231] Preferred binder polymers include linear organic polymers. Linear organic polymers which are soluble or swellable in water or a weak alkali solution in water are preferred. Of these, (meth)acrylic resins having unsaturated groups (e.g., allyl, acryloyl) or benzyl groups and carboxy groups in side chains are especially preferred because they provide an excellent balance of film strength, sensitivity and developability.

[0232] Radical-polymerizable compounds and binder polymers that may be used include those described specifically in paragraphs [0036] to [0060] of JP 2001-133969 A.

[0233] Thermal negative-type photosensitive compositions preferably contain additives described in paragraphs [0061] to [0068] of JP 2001-133969 A (e.g., surfactants for enhancing coatability).

[0234] The methods described in detail in JP 2001-133969 A may be used to form a polymerizable layer and to make a printing plate having such a layer.

<Acid-crosslinkable layer>

[0235] Another preferred thermal negative-type image recording layer is an acid-crosslinkable image recording layer (abbreviated hereinafter as "acid-crosslinkable layer"). An acid-crosslinkable layer contains a photothermal conversion substance, a thermal acid generator, a compound (crosslinker) which is curable and which crosslinks under the influence of an acid, and an alkali-soluble polymeric compound which is capable of reacting with the crosslinker in the presence of an acid. In an acid-crosslinkable layer, the photothermal conversion substance converts absorbed infrared light into heat. The heat decomposes the thermal acid generator, thereby generating an acid which causes the crosslinker and the alkali-soluble polymeric compound to react and cure.

[0236] The photothermal conversion substance is exemplified by the same substances as can be used in the polymerizable layer.

[0237] Exemplary thermal acid generators include photoinitiators for photopolymerization, dye photochromogenic substances, and heat-decomposable compounds such as acid generators which are used in microresists and the like.

[0238] Exemplary crosslinkers include hydroxymethyl- or alkoxymethyl-substituted aromatic compounds, compounds having N-hydroxymethyl, N-alkoxymethyl or N-acyloxymethyl groups, and epoxy compounds.

[0239] Exemplary alkali-soluble polymeric compounds include novolak resins and polymers having hydroxyaryl groups in side chains.

<Photopolymer-Type Photosensitive Compositions>

[0240] Photopolymer-type photosensitive compositions contain an addition-polymerizable compound, a photopolymerization initiator and a polymer binder.

[0241] Preferred addition-polymerizable compounds include compounds containing an ethylenically unsaturated bond which are addition-polymerizable. Ethylenically unsaturated bond-containing compounds are compounds which have a terminal ethylenically unsaturated bond. Such compounds may have the chemical form of a monomer, a prepolymer, or a mixture thereof. The monomers are exemplified by esters of unsaturated carboxylic acids (e.g., acrylic acid, methacrylic acid, itaconic acid, maleic acid) and aliphatic polyols, and amides of unsaturated carboxylic acids and aliphatic polyamines.

[0242] Preferred addition-polymerizable compounds include also urethane-type addition-polymerizable compounds.

[0243] The photopolymerization initiator may be any of various photopolymerization initiators or a system of two or more photopolymerization initiators (photoinitiation system) which is suitably selected according to the wavelength of the light source to be used. Preferred examples include the initiatzon systems described in paragraphs [0021] to [0023] of JP 2001-22079 A.

[0244] The polymer binder, inasmuch as it must function as a film-forming agent for the photopolymerizable photosensitive composition and, at the same time, must allow the image recording layer to dissolve in an alkaline developer, should be an organic polymer which is soluble or swellable in an aqueous alkali solution. Preferred examples of such organic polymers include those described in paragraphs [0036] to [0063] of JP 2001-22079 A.

[0245] It is preferable for the photopolymer-type photosensitive composition to include the additives described in paragraphs [0079] to [0088] of JP 2001-22079 A (e.g., surfactants for improving coatability, colorants, plasticizers, thermal polymerization inhibitors).

[0246] To prevent the inhibition of polymerization by oxygen, it is preferable to provide an oxygen-blocking protective layer on top of the photopolymer-type image recording layer. The polymer present in the oxygen-blocking protective layer is exemplified by polyvinyl alcohols and copolymers thereof.

[0247] It is also desirable to provide an intermediate layer or a bonding layer like those described in paragraphs [0124] to [0165] of JP 2001-228608 A.

<Conventional Negative-Type Photosensitive Compositions>

[0248] Conventional negative-type photosensitive compositions contain a diazo resin or a photo-crosslinkable resin. Among others, photosensitive compositions which contain a diazo resin and an alkali-soluble or -swellable polymeric compound (binder) are preferred.

[0249] The diazo resin is exemplified by condensation products of an aromatic diazonium salt with an active carbonyl group-bearing compound such as formaldehyde; and organic solvent-soluble diazo resin inorganic salts which are the reaction products of a hexafluorophosphate or tetrafluoroborate with the condensation product of a p-diazophenylamine and formaldehyde. The high-molecular-weight diazo compounds described in JP 59-78340 A, in which the content of hexamer and larger polymers is at least 20 mol%, are especially preferred.

[0250] Exemplary binders include copolymers containing acrylic acid, methacrylic acid, crotonic acid or maleic acid as an essential component. Specific examples include the multi-component copolymers of such monomers as 2-hydroxyethyl (meth)acrylate, (meth)acrylonitrile and (meth)acrylic acid described in JP 50-118802 A, and the multi-component copolymers of alkyl acrylates, (meth)acrylonitrile and unsaturated carboxylic acids described in JP 56-4144 A.

[0251] Conventional negative-type photosensitive compositions preferably contain as additives the print-out agents, dyes, plasticizers for imparting flexibility and wear resistance to the applied coat, development promoters and other compounds, and the surfactants for enhancing coatability described in paragraphs [0014] to [0015] of JP 7-281425 A.

[0252] Below the conventional negative-type photosensitive layer, it is advantageous to provide the intermediate layer which contains a polymeric compound having an acid group-bearing component and an onium group-bearing component described in JP 2000-105462 A.

<Conventional Positive-Type Photosensitive Compositions>

[0253] Conventional positive-type photosensitive compositions contain a quinonediazide compound. Photosensitive compositions containing an o-quinonediazide compound and an alkali-soluble polymeric compound are especially preferred.

[0254] Illustrative examples of the o-quinonediazide compound include esters of 1,2-naphthoquinone-2-diazido-5-sulfonylchloride and a phenol-formaldehyde resin or a cresol-formaldehyde resin, and the esters of 1,2-naphthoquinone-2-diazido-5-sulfonylchloride and pyrogallol-acetone resins described in US 3,635,709.

[0255] Illustrative examples of the alkali-soluble polymeric compound include phenol-formaldehyde resins, cresol-formaldehyde resins, phenol-cresol-formaldehyde co-condensation resins, polyhydroxystyrene, N-(4-hydroxyphenyl)methacrylamide copolymers, the carboxy group-bearing polymers described in JP 7-36184 A, the phenolic hydroxy group-bearing acrylic resins described in JP 51-34711 A, the sulfonamide group-bearing acrylic resins described in JP 2-866 A, and urethane resins.

[0256] Conventional positive-type photosensitive compositions preferably contain as additives the compounds such as sensitivity regulators, print-out agents and dyes described in paragraphs [0024] to [0027] of JP 7-92660 A, and surfactants for enhancing coatability such as are described in paragraph [0031] of JP 7-92660 A.

[0257] Below the conventional positive-type photosensitive layer, it is advantageous to provide an intermediate layer similar to the intermediate layer which is preferably used in the case of the conventional negative-type photosensitive layer as above.

<Non-Treatment Type Photosensitive Compositions>

[0258] Illustrative examples of non-treatment type photosensitive compositions include thermoplastic polymer powder-based photosensitive compositions, microcapsule-based photosensitive compositions, and sulfonic acid-generating polymer-containing photosensitive compositions. All of these are heat-sensitive compositions containing a photothermal conversion substance. The photothermal conversion substance is preferably a dye of the same type as those which can be used in the above-described thermal positive-type photosensitive compositions.

[0259] Thermoplastic polymer powder-based photosensitive compositions are composed of a hydrophobic, heat-meltable finely divided polymer dispersed in a hydrophilic polymer matrix. In the thermoplastic polymer powder-based image recording layer, the fine particles of hydrophobic polymer melt under the influence of heat generated by light exposure and mutually fuse, forming hydrophobic regions which serve as the image areas.

[0260] The finely divided polymer is preferably one in which the particles melt and fuse together under the influence of heat. A finely divided polymer in which the individual particles have a hydrophilic surface, enabling them to disperse in a hydrophilic component such as fountain solution, is especially preferred. Preferred examples include the finely divided thermoplastic polymers described in Research Disclosure No. 33303 (January 1992), JP 9-123387 A, JP 9-131850 A, JP 9-171249 A, JP 9-171250 A and EP 931,647 A. Of these, polystyrene and polymethyl methacrylate are preferred. Illustrative examples of finely divided polymers having a hydrophilic surface include those in which the polymer itself is hydrophilic, and those in which the surfaces of the polymer particles have been rendered hydrophilic by adsorbing thereon a hydrophilic compound such as polyvinyl alcohol or polyethylene glycol.

[0261] The finely divided polymer preferably has reactive functional groups.

[0262] Preferred examples of microcapsule-type photosensitive compositions include those described in JP 2000-118160 A, and compositions like those described in JP 2001-277740 A in which a compound having thermally reactive functional groups is enclosed within microcapsules.

[0263] Illustrative examples of sulfonic acid-generating polymers that may be used in sulfonic acid generating polymer-containing photosensitive compositions include the polymers described in JP 10-282672 A that have sulfonate ester groups, disulfone groups or sec- or tert-sulfonamide groups in side chains.

[0264] Including a hydrophilic resin in a non-treatment type photosensitive composition not only provides a good on-press developability, it also enhances the film strength of the photosensitive layer itself. Preferred hydrophilic resins include resins having hydrophilic groups such as hydroxy, carboxy, hydroxyethyl, hydroxypropyl, amino, aminoethyl, aminopropyl or carboxymethyl groups; and hydrophilic binder resins of a sol-gel conversion-type.

[0265] A non-treatment type image recording layer can be developed on the press, and thus does not require a special development step. The methods described in detail in JP 2002-178655 A may be used as the method of forming a non-treatment type image recording layer and the associated platemaking and printing methods.

<Back Coat>

[0266] If necessary, the presensitized plate of the invention obtained by providing any of the various above image recording layers on a lithographic printing plate support obtained according to the invention may be provided on the rear side with a coat composed of an organic polymeric compound to prevent scuffing of the image recording layer when the presensitized plates are stacked on top of each other.

[Lithographic Platemaking Process]

[0267] A lithographic printing plate is prepared from the presensitized plate comprising a lithographic printing plate support obtained according to this invention by any of various treatment methods, depending on the type of image recording layer.

[0268] Illustrative examples of sources of actinic light that may be used for imagewise exposure include mercury vapor lamps, metal halide lamps, xenon lamps and chemical lamps. Examples of laser beams that may be used include those from helium-neon lasers (He-Ne lasers), argon lasers, krypton lasers, helium-cadmium lasers, KrF excimer lasers, semiconductor lasers, YAG lasers and YAG-SHG lasers.

[0269] Following the above exposure, if the image recording layer is of a thermal positive type, thermal negative type, conventional negative type, conventional positive type or photopolymer type, it is preferable to carry out development using a developer in order to prepare a lithographic printing plate.

[0270] The developer is preferably an alkaline developer, and more preferably an alkaline aqueous solution which is substantially free of organic solvent.

[0271] Developers which are substantially free of alkali metal silicates are also preferred. One example of a suitable method of development using a developer which is substantially free of alkali metal silicates is the method described in detail in JP 11-109637 A.

[0272] Developers which contain an alkali metal silicate may also be used.

EXAMPLES

[0273] Hereinafter, the present invention is described in detail with reference to non-limitative examples.

1. Manufacture of Aluminum Plate Embossing Roll

[0274] A roll of tool steel (SKD11) that had been quenched to a hardness of Hv750 was successively subjected to treatments (1) to (5) below, yielding an aluminum plate embossing roll.

(1) Mirror Polishing

[0275] Buffing was carried out as the mirror polishing process, thereby removing marks left by the grindstone used to abrade the surface of the roll. Of the buffed surface, the average roughness R_a was 0.2 μm and the maximum height R_{max} was 1μm. The average roughness R_a and the maximum height R_{max} were measured according to the measurement procedures for the arithmetic mean deviation of the profile R_a and maximum height of the profile Ry defined in JIS B0601-1994.

(2) Blasting

[0276] The roll surface was subjected to graining treatment by air blasting it twice using a grit material composed of #80 mesh alumina particles. Each blast was carried out at an air pressure of 2 kgf/cm^2 (1.96×10^5 Pa) and the average roughness R_a of the air-blasted surface was 0.8 μm.

(3) Degreasing

[0277] The roll was immersed for 30 seconds in a 30°C degreaser liquid contained in a degreasing tank, and oil on the roll surface was removed with the liquid. The roll was then rinsed with water, after which air was blown over it to remove moisture.

(4) Electrolytic Treatment

[0278] The roll was subjected to electrolytic treatment by the application of continuous direct current to the roll as an anode in a 50°C electrolyte solution containing 300 g/L of chromic acid, 2 g/L of sulfuric acid and 1 g/L of iron at a current density of 30 A/dm^2. The amount of electricity used in the electrolytic treatment was 10,000 C/dm^2.

[0279] The direct current was provided by the three-phase full-wave rectification of current waveform and then passed through a filter circuit before application so as to reduce its ripple component to 5% or less. Lead was used as the counter electrode. The roll was placed upright in the electrolyte solution, and the lead electrode was arranged in a cylindrical form so as to encircle it. The shaft portion of the roll was masked with vinyl chloride to keep it from undergoing electrolytic treatment.

(5) Chromium Plating

[0280] Next, chromium plating treatment was performed on the roll by the application of direct current to the roll as a cathode in a 50°C electrolyte solution containing 300 g/L of chromic acid, 2 g/L of sulfuric acid and 1 g/L of iron at a current density of 40 A/dm^2. The plating treatment time was so set as to give a plating thickness of 6 μm.

[0281] The direct current was provided by the three-phase full-wave rectification of current waveform and then passed through a filter circuit before application so as to reduce its ripple component to 5% or less. Lead was used as the counter electrode. The roll was placed upright in the electrolyte solution, and the lead electrode was arranged in a cylindrical form so as to encircle it. The shaft portion of the roll was masked with vinyl chloride to keep it from undergoing plating treatment.

2. Fabrication of Aluminum Plate

[0282] A melt was prepared from an aluminum alloy comprising the respective components (wt%) shown in Table 1, with the balance being aluminum and inevitable impurities. The aluminum alloy melt was subjected to molten metal treatment and filtration, then was cast into a 500 mm thick, 1,200 mm wide ingot by a direct chill casting process. The ingot was scalped with a scalping machine, removing about 10 mm of material from the surface, then soaked and held at 550°C for about 5 hours. When the temperature had fallen to 400°C, the ingot was rolled with a hot rolling mill to a thickness of 2.7 mm. In addition, heat treatment was carried out at 500°C in a continuous annealing furnace, and cold rolling was carried out, whereby the aluminum plate was finished to a thickness of 0.3 mm and a width of 1,060 mm. In this way, aluminum plates 1 to 3 were obtained.

[0283] Aluminum plates 4 to 6 were obtained by repeating the method used for the aluminum plates 1 to 3, respectively, except that the aluminum plate embossing roll obtained as above was used in the cold rolling.

Table 1

Aluminum plate	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
1	0.080	0.300	0.001	0.001	0.000	0.001	0.003	0.021
2	0.076	0.270	0.023	0.001	0.000	0.001	0.003	0.021
3	0.278	0.413	0.201	0.892	0.783	0.022	0.122	0.034

3. Fabrication of Lithographic Printing Plate Support

Examples 1-1 to 1-38, 3-1 to 3-7, 3-9, and Comparative Examples 1-1 and 1-2

[0284] The aluminum plates obtained in the above processes were subjected to surface treatments described below to obtain the lithographic printing plate supports shown in Table 2.

<Surface Treatment>

[0285] The aluminum plates were successively subjected to the following surface treatments (a) to (g).

(a) Etching in Aqueous Alkali Solution (First Etching Treatment)

[0286] Etching was carried out by spraying the aluminum plates with an aqueous solution having a sodium hydroxide concentration of 370 g/L, an aluminum ion concentration of 100 g/L and a temperature of 60°C from a spray line. The amount of material removed by etching from the surface of each aluminum plate to be subsequently subjected to electrochemical graining treatment was 3 g/m^2.

[0287] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(b) Desmutting in Aqueous Acidic Solution (First Desmutting Treatment)

[0288] Desmutting was carried out for 5 seconds by spraying the aluminum plates with an aqueous solution having 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 line. Wastewater from the subsequently described anodizing treatment step (f) was used here as the aqueous sulfuric acid solution.

[0289] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(c) Electrochemical Graining with Alternating Current in Aqueous Acidic Solution (Electrochemical Graining Treatment)

[0290] Electrochemical graining was carried out with respect to the aluminum plates subjected to the treatment (b) by using aqueous solutions having chloride ion concentrations, nitrate ion concentrations, aluminum ion concentrations and pH values shown in Table 2 (temperature: 35°C) as the electrolyte solutions, controlling the current through inverter control using an IGBT device, and utilizing a power supply capable of generating an alternating current of any waveform.

[0291] The chloride ion concentration was adjusted using hydrochloric acid and/or aluminum chloride, the nitrate ion concentration was adjusted using nitric acid, and the aluminum ion concentration was adjusted using aluminum chloride.

[0292] The waveform of the current used, rise time when the current has a trapezoidal waveform, frequency of the current used, amount of electricity, and current ratio were as shown in Table 2. The amount of electricity refers to the total amount of electricity when the aluminum plate to be treated serves as an anode. The current ratio refers to the ratio between the total amount of electricity when the aluminum plate to be treated serves as a cathode and the total amount of electricity when the plate serves as an anode.

[0293] At the alternating current peaks, the current density when the aluminum plate to be treated serves as an anode was 50 A/dm^2. The duty ratio was 0.5.

[0294] For the concentration control of the electrolyte solutions, a method was used in which chloride ion, nitrate ion and water were added in amounts proportional to the amount of applied electricity according to the predetermined data table, multi-component concentration measurement was carried out by the capillary electrophoretic analysis and the amounts of chloride ion, nitrate ion and water to be added were corrected based on the obtained results.

[0295] At the end of the treatment, the solutions were removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(d) Etching in Aqueous Alkali Solution (Second Etching Treatment)

[0296] Etching was carried out by spraying the aluminum plates with an aqueous solution having a sodium hydroxide concentration of 50 g/L, an aluminum ion concentration of 5 g/L and a temperature of 35°C from a spray line. The amount of materials removed by etching from the surfaces of the aluminum plates subjected to the electrochemical graining treatment was as shown in Table 2.

[0297] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(e) Desmutting in Aqueous Acidic Solution (Second Desmutting Treatment)

[0298] Desmutting was carried out for 5 seconds by spraying the aluminum plates with an aqueous solution having 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 line. Wastewater from the subsequently described anodizing treatment step (f) was used here as the aqueous sulfuric acid solution.

[0299] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(f) Anodizing Treatment

[0300] The electrolyte solution used was prepared by dissolving aluminum sulfate in a 170 g/L aqueous sulfuric acid solution to an aluminum ion concentration of 5 g/L, and had a temperature of 50°C. Anodizing treatment was carried out in such a way that the average current density during the anodic reaction of the aluminum plate to be treated was 15 A/dm^2. The final weight of the anodized layer was 2.7 g/m^2.

[0301] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers.

(g) Hydrophilizing Treatment

[0302] Hydrophilizing treatment was carried out by immersing the aluminum plates in a 1 wt% solution of sodium silicate in water (solution temperature: 20°C) for 10 seconds. The amount of silicon on the surface of each aluminum plate, as measured by a fluorescent x-ray analyzer, was 3.5 mg/m^2.

[0303] The solution was removed from the plates with nip rollers. Rinsing treatment was then carried out for 5 seconds using fanned-out sprays of water from spray tips mounted on spray lines, and the rinse water was removed from the plates with nip rollers. After that, the aluminum plates were dried by blowing 90°C air thereon for 10 seconds, thereby giving the lithographic printing plate supports.

Examples 2-1 to 2-4 and 3-8

[0304] The lithographic printing plate supports of Examples 2-1 to 2-4 and 3-8 in Table 2 were obtained by the same method as in Examples 1-1 to 1-38 except that the treatment (z) to be described below was carried out prior to the treatment (a) and, in (a), the amount of material removed by etching from the surface of each aluminum plate to be subsequently subjected to electrochemical graining treatment was 10 g/m^2.

(z) Mechanical Graining Treatment

[0305] Using an apparatus as shown in FIG. 6, mechanical graining treatment was carried out with rotating nylon roller brushes while a suspension of an abrasive (pumice) in water (specific gravity: 1.12) was supplied to the surface of the aluminum plate to be treated as an abrasive slurry. FIG. 6 shows an aluminum plate 1, roller brushes 2 and 4, an abrasive slurry 3, and support rollers 5, 6, 7 and 8. The average particle size of the abrasive was 30 μm. The brushes comprised bristles made of nylon 6.10 and having a length of 50 mm and a diameter of 0.3 mm. In each brush, the nylon bristles were densely set in the holes formed in a stainless steel cylinder with a diameter of 300 mm. The rotating brushes used were three in number. Two support rollers (200 mm diameter) were situated below each brush and spaced 300 mm apart. The direction in which the brushes were rotated was the same as the direction of advance of the aluminum plate. The speed of rotation of the brushes was 200 rpm. The average roughness R_a of a mechanically grained surface was 0.45 μm.

4. Surface Examination of Lithographic Printing Plate Support

[0306] The surface profile of the lithographic printing plate supports obtained in Examples 1-1 to 1-38, 2-1 to 2-4 and 3-1 to 3-4 was examined under a scanning electron microscope (JSM-5500 manufactured by JEOL, Ltd.; the same applies below) at a magnification of 50,000X, whereupon fine recesses with a diameter of 0.01 to 0.5 μm were found to have uniformly and densely been formed on the surface of each support. In addition, it was found upon the examination under the scanning electron microscope at a magnification of 2,000X that recesses with a diameter of 1 to 5 μm had been formed on the surfaces of the lithographic printing plate supports. The fine recesses with a diameter of 0.01 to 0.5 μm were superimposed on the recesses with a diameter of 1 to 5 μm. The recesses with a diameter of 1 to 5 μm were generally separate from one another and had uniformity.

[0307] On the other hand, the surface profile of the lithographic printing plate supports obtained in Comparative Examples 1 and 2 was also examined in the same manner, and fine recesses with a diameter of 0.01 to 0.5 μm and recesses with a diameter of 1 to 5 μm were found to have been formed on the surface of each support. The recesses with a diameter of 1 to 5 μm, however, were overlapping on their edges more frequently than in the above Examples and lacked uniformity.

5. Fabrication of Presensitized Plate

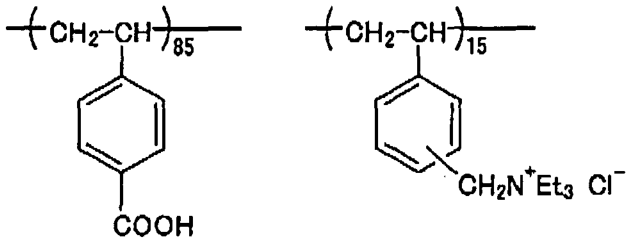
[0308] Presensitizod plates for lithographic printing were fabricated by providing a thermal positive-type image recording layer in the manner described below on the respective lithographic printing plate supports obtained as above. Before providing the image recording layer, an undercoat was formed on the support as follows.

[0309] An undercoating solution of the composition indicated below was applied onto the lithographic printing plate support and dried at 80°C for 15 seconds, thereby forming an undercoat layer. The weight of the undercoat layer after drying was 15 mg/m^2.

Composition of Undercoating Solution

[0310]

Polymeric compound of the following formula	0.3 g



molecular weight: 28,000

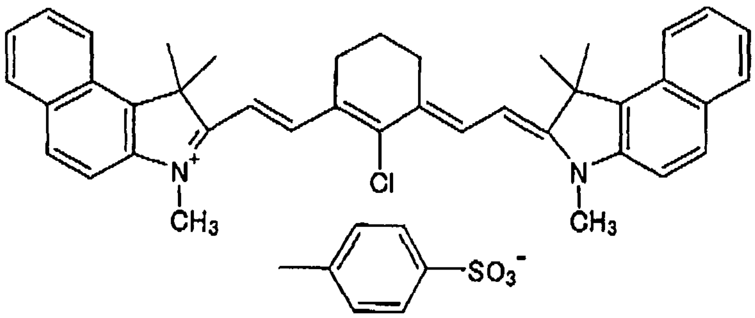
Methanol	100 g
Water	1 g

[0311] Next, a heat-sensitive layer-forming coating solution of the following composition was prepared and applied onto the undercoated lithographic printing plate support to a coating weight (heat-sensitive layer weight) after drying of 1.8 g/m^2. As a result of subsequent drying, a heat-sensitive layer (thermal positive-type image recording layer) was formed and a presensitized plate was thus obtained.

Composition of Heat-Sensitive Layer-Forming Coating Solution

[0312]

Novolak resin (m-cresol/p-cresol = 60/40; weight-average molecular weight, 7,000; unreacted cresol content, 0.5 wt%)	0.90 g
Ethyl methacrylate/isobutyl methacrylate/methacrylic acid copolymer (molar ratio, 35/35/30)	0.10 g
Cyanine dye A of the following formula	0.1 g



Cyanine Dye A

Tetrahydrophthalic anhydride	0.05 g
p-Toluenesulfonic acid	0.002 g
Ethyl violet in which counterion was 6-hydroxy-β-naphthalenesulfonic acid	0.02 g
Fluorochemical surfactant (Megaface F-780F, product of Dainippon Ink and Chemicals, Inc.; 30 wt% solids)	0.0045 g (as solids)
Fluorochemical surfactant (Megaface F-781F, product of Dainippon Ink and Chemicals, Inc.; 100 wt% solids)	0.035 g
Methyl ethyl ketone	12 g

6. Evaluation of Presensitized Plate

[0313] The resulting presensitized plates were evaluated on the basis of the press life, scumming resistance and shininess of the lithographic printing plates prepared from them. Evaluation methods were as follows.

(1) Press Life

[0314] Trendsetter manufactured by Creo was used to form an image on the presensitized plate at a drum rotation speed of 150 rpm and a beam intensity of 10 W.

[0315] The presensitized plates were then developed with PS Processor 940H manufactured by Fuji Photo Film Co., Ltd. that was charged with an alkaline developer of the following composition so as to obtain lithographic printing plates. During the development, the temperature of the developer was kept to 30°C and the developing time was set to 20 seconds. The presensitized plates were all excellent in sensitivity.

Composition of Alkaline Developer

[0316]

D-sorbitol	2.5 wt%
Sodium hydroxide	0.85 wt%
Polyethylene glycol lauryl ether (weight-average molecular weight: 1,000)	0.5 wt%

Table continued

Water	96.15 wt%

[0317] Printing was carried out with the obtained lithographic printing plates on a Lithrone printing press manufactured by Komori Corporation using DIC-GEOS (N) black ink, a product of Dainippon Ink and Chemicals, Inc. The press life of each printing plate was evaluated based on the number of the printed sheets which had already been made from the relevant plate at the time when the decrease in density of a solid image became visually recognizable. Naturally, a larger number implied a better press life.

[0318] Results are shown in Table 2. Meanings of the letters in the table are as follows.

A: The number was 30,000 or more.
A-B: The number was 20,000 or more but less than 30,000.
B: The number was 10,000 or more but less than 20,000.
C: The number was less than 10,000.

(2) Scumming Resistance

[0319] With the lithographic printing plates obtained in the same manner as in the evaluation of press life as described in (1) above, printing was carried out on a Mitsubishi DAIYA F2 printing press (manufactured by Mitsubishi Heavy Industries, Ltd.) using DIC-GEOS (s) magenta ink. The scumming resistance of each printing plate was evaluated by visually inspecting the blanket for stains after ten thousand printed sheets had been made from the relevant plate.

[0320] Results are shown in Table 2. Meanings of the letters in the table are as follows.

A: The blanket had almost no stains.
A-B: The blanket had few stains.
B: The blanket had tolerable stains.
C: The blanket was certainly stained and the printed sheets underwent evident scumming.

(3) Shininess

[0321] The lithographic printing plates obtained in the same manner as in the evaluation of press life as described in (1) above were set on a Lithrone printing press manufactured by Komori Corporation and the state of shining in non-image areas of the surface of each printing plate was visually inspected while supplying a fountain solution little by little. The shininess (the ease with which the amount of fountain solution on the plate surface can be perceived) of each printing plate was evaluated in terms of the amount of the fountain solution which had been supplied when the plate surface began to shine.

[0322] Results are shown in Table 2. Meanings of the letters in the table are as follows.

A: The plate surface did not shine until the fountain solution supplied little by little became substantially large in total amount.
B: The plate surface already shone when the fountain solution supplied little by little was still small in total amount so that it was a bit difficult to adjust the amount of fountain solution under visual inspection.

[0323] As is evident from Table 2, every lithographic printing plate using any of the lithographic printing plate supports obtained by the method of manufacturing a lithographic printing plate support according to the present invention (Examples 1-1 to 1-38, 2-1 to 2-4 and 3-1 to 3-4) had a good press life and excellent scumming resistance. The shininess was also excellent.

[0324] Moreover, in the cases where an aluminum plate embossing roll was pressed onto the surface of an aluminum plate before the first etching treatment so as to impart recessed and protruded portions thereto (Examples 1-1 to 1-18 and 1-37) and where an aluminum plate was subjected to the mechanical graining treatment before the first etching treatment so as to impart recessed and protruded portions to the surface thereof (Examples 2-1 to 2-4 and 3-8), the lithographic printing plate using any of the obtained lithographic printing plate supports was particularly excellent in shininess.

[0325] On the other hand, in Comparative Example 1-1 in which too large a total amount of electricity when the aluminum plate serves as an anode was employed for the electrochemical graining treatment, the lithographic printing plate using the obtained lithographic printing plate support was inferior in scumming resistance.

[0326] In Comparative Example 1-2 in which the pH of the aqueous solution employed in the electrochemical graining treatment was too high, the obtained lithographic printing plate support had pits formed thereon which were inadequately dispersed and not uniform in size to actually generate large recesses. The lithographic printing plate using the support was inferior not only in scumming resistance but also press life and shininess.

TABLE 2

	Al Plate	Mechanical graining	First etching	Electrochemical graining												Second etching	Printing performance		
			Amount of dissolved Al (g/m^2)	Waveform	[HCl] (g/L)	[Cl^-] (g/L)	[HNO_3] (g/L)	[NO_3^-] (g/L)	[Al^{3+}] (g/L)	pH	Current rise time (msec)	Amount of electricity (C/dm^2)	Duty ratio	Current ratio	Frequency (Hz)	Amount of dissolved Al (g/m^2)	Press life	Scumming resistance	Shininess
Ex.1-1	4	Not done	3	Sinusoidal	7.5	11.3	1.0	0.98	5.0	0.78	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-2	4	Not done	3	Sinusoidal	7.5	11.3	3.0	2.95	5.0	0.73	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-3	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-4	4	Not done	3	Sinusoidal	7.5	11.3	8.0	7.87	5.0	0.60	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-5	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.05	A	B	A
Ex.1-6	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.20	A-B	A	A
Ex.1-7	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.30	A-B	A	A
Ex.1-8	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.50	A-B	A	A
Ex.1-9	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	1.00	B	A	A
Ex.1-10	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	1.00	60	0.10	A	A	A
Ex.1-11	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	1.00	50	0.10	A	A	A
Ex.1-12	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	100	0.5	0.95	60	0.10	B	A	A
Ex.1-13	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	150	0.5	0.95	60	0.10	A-B	A	A
Ex.1-14	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	250	0.5	0.95	60	0.10	A	A	A
Ex.1-15	4	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	300	0.5	0.95	60	0.10	A	A-B	A
Ex.1-16	5	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-17	6	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.1-18	4	Not done	3	Trapezoidal	7.5	11.3	5.0	4.92	5.0	0.68	0.8	200	0.5	0.95	60	0.10	A	A	A
Ex.1-19	1	Not done	3	Sinusoidal	7.5	11.3	1.0	0.98	5.0	0.78	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-20	1	Not done	3	Sinusoidal	7.5	11.3	3.0	2.95	5.0	0.73	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-21	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-22	1	Not done	3	Sinusoidal	7.5	11.3	8.0	7.87	5.0	0.60	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-23	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.05	A	B	B
Ex.1-24	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.20	A-B	A	B
Ex.1-25	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.30	A-B	A	B

TABLE 2 (continued)

	Al Plate	Mechanical graining	First etching	Electrochemical graining												Second etching	Printing performance		
			Amount of dissolved Al (g/m^2)	Wave-form	[HCl] (g/L)	[Cl^-] (g/L)	[HNO_3] (g/L)	[NO_3^-] (g/L)	[Al^{3+}] (g/L)	pH	Current rise time (msec)	Amount of electricity (C/dm^2)	Duty ratio	Current ratio	Frequency (Hz)	Amount of dissolved Al (g/m^2)	Press life	Scumming resistance	Shininess
Ex.1-26	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.50	A-B	A	B
Ex.1-27	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	1.00	B	A	B
Ex.1-28	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	1.00	60	0.10	A	A	B
Ex.1-29	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	1.00	50	0.10	A	A	B
Ex.1-30	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	100	0.5	0.95	60	0.10	B	A	B
Ex.1-31	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	150	0.5	0.95	60	0.10	A-B	A	B
Ex.1-32	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	250	0.5	0.95	60	0.10	A	A	B
Ex.1-33	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	300	0.5	0.95	60	0.10	A	A-B	B
Ex.1-34	2	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-35	3	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	B
Ex.1-36	1	Not done	3	Trapezoidal	7.5	11.3	5.0	4.92	5.0	0.68	0.8	200	0.5	0.95	60	0.10	A	A	B
Ex.1-37	4	Not done	3	Triangular	10.0	16.1	5.0	4.92	8.0	0.54	17	295	0.5	0.95	30	0.20	A	A	A
Ex.1-38	1	Not done	3	Triangular	10.0	16.1	5.0	4.92	8.0	0.54	14	295	0.5	0.95	30	0.20	A	A	B
Ex.2-1	1	Done	10	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.2-2	2	Done	10	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.2-3	3	Done	10	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	200	0.5	0.95	60	0.10	A	A	A
Ex.2-4	2	Done	10	Trapezoidal	7.5	11.3	5.0	4.92	5.0	0.68	0.8	200	0.5	0.95	60	0.10	A	A	A
Ex.3-1	1	Not done	3	Sinusoidal	7.5	24.5	5.0	4.50	4.5	0.43	-	200	0.5	0.95	60	0.10	A	A-B	B
Ex.3-2	1	Not done	3	Sinusoidal	0.0	52.0	13.0	12.00	13.5	0.45	-	200	0.5	0.95	60	0.10	A	B	B
Ex.3-3	1	Not done	3	Sinusoidal	7.5	24.5	3.0	2.70	4.5	0.46	-	200	0.5	0.95	60	0.10	A-B	A	B
Ex.3-4	1	Not done	3	Sinusoidal	7.5	24.5	1.0	0.90	4.5	0.51	-	200	0.5	0.95	60	0.10	A-B	A	B
Ex.3-5	4	Not done	3	Sinusoidal	7.5	24.5	5.0	4.50	4.5	0.43	-	200	0.5	0.95	60	0.10	A	A	A
Ex.3-6	2	Not done	3	Sinusoidal	7.5	24.5	5.0	4.50	4.5	0.43	-	200	0.5	0.95	60	0.10	A	A-B	A
Ex.3-7	3	Not done	3	Sinusoidal	7.5	24.5	5.0	4.50	4.5	0.43	-	200	0.5	0.95	60	0.10	A	B	A
Ex.3-9	1	Done	3	Sinusoidal	7.5	24.5	5.0	4.50	4.5	0.43	-	200	0.5	0.95	60	0.10	A	A-B	A
Ex.3-8	1	Not done	3	Sinusoidal	0.0	7.0	1.0	1.00	1.8	1.56	-	200	0.5	0.95	60	0.10	B	B	B
CEx.1-1	1	Not done	3	Sinusoidal	7.5	11.3	5.0	4.92	5.0	0.68	-	900	0.5	0.95	60	0.10	C	C	A
CEx.1-2	1	Not done	3	Sinusoidal	0.0	7.0	0.0	0.00	1.8	2.70	-	200	0.5	0.95	60	0.10	C	C	C

Claims

1. A method of manufacturing a lithographic printing plate support comprising a step of subjecting an aluminum plate to an electrochemical graining treatment in which alternating current is passed through the aluminum plate in an aqueous solution containing at least chloride ion and nitrate ion so that total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm^2.

2. The method of manufacturing a lithographic printing plate support according to claim 1, wherein the aqueous solution contains hydrochloric acid and nitric acid.

3. The method of manufacturing a lithographic printing plate support according to claim 1 or 2, wherein the aqueous solution has a chloride ion concentration of 3 g/L or more and a nitrate ion concentration of 0.50 g/L or more.

4. The method of manufacturing a lithographic printing plate support according to any one of claims 1 to 3, wherein the aqueous solution has a pH of 0.8 or less.

5. The method of manufacturing a lithographic printing plate support according to any one of claims 1 to 4, wherein the aqueous solution contains 2 g/L or more of aluminum ions.

6. The method of manufacturing a lithographic printing plate support according to any one of claims 1 to 5, wherein the aluminum plate has a pattern of recessed and protruded portions provided on its surface.

FIG.1

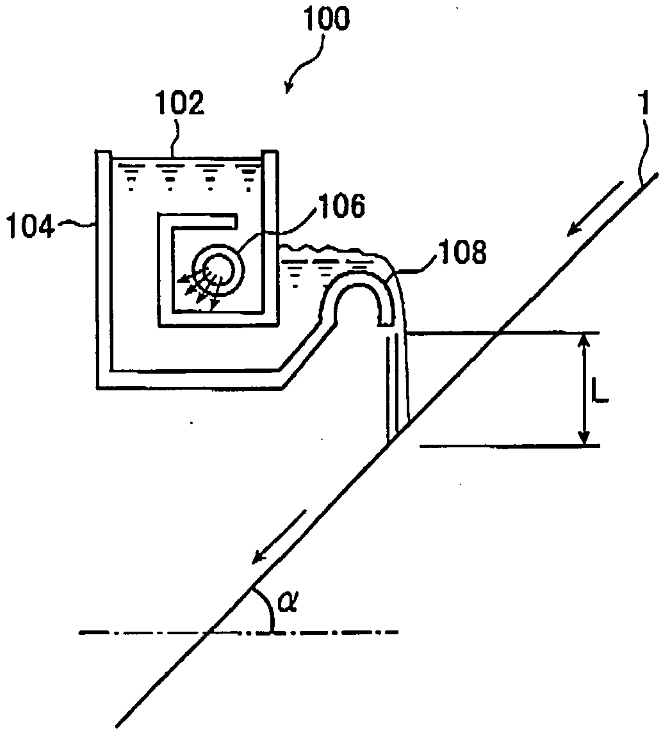


FIG.2

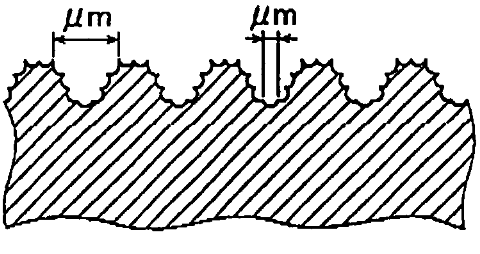


FIG.3

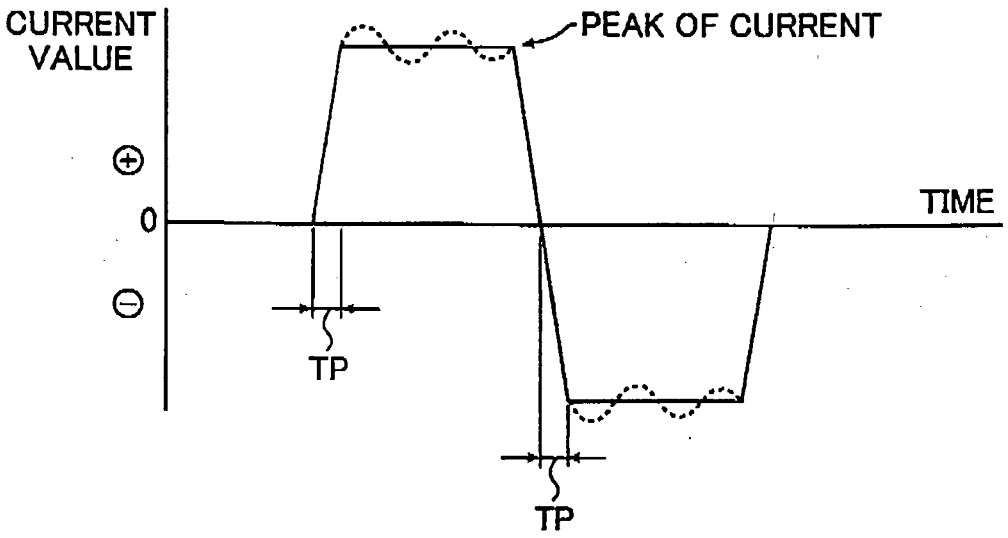


FIG.4

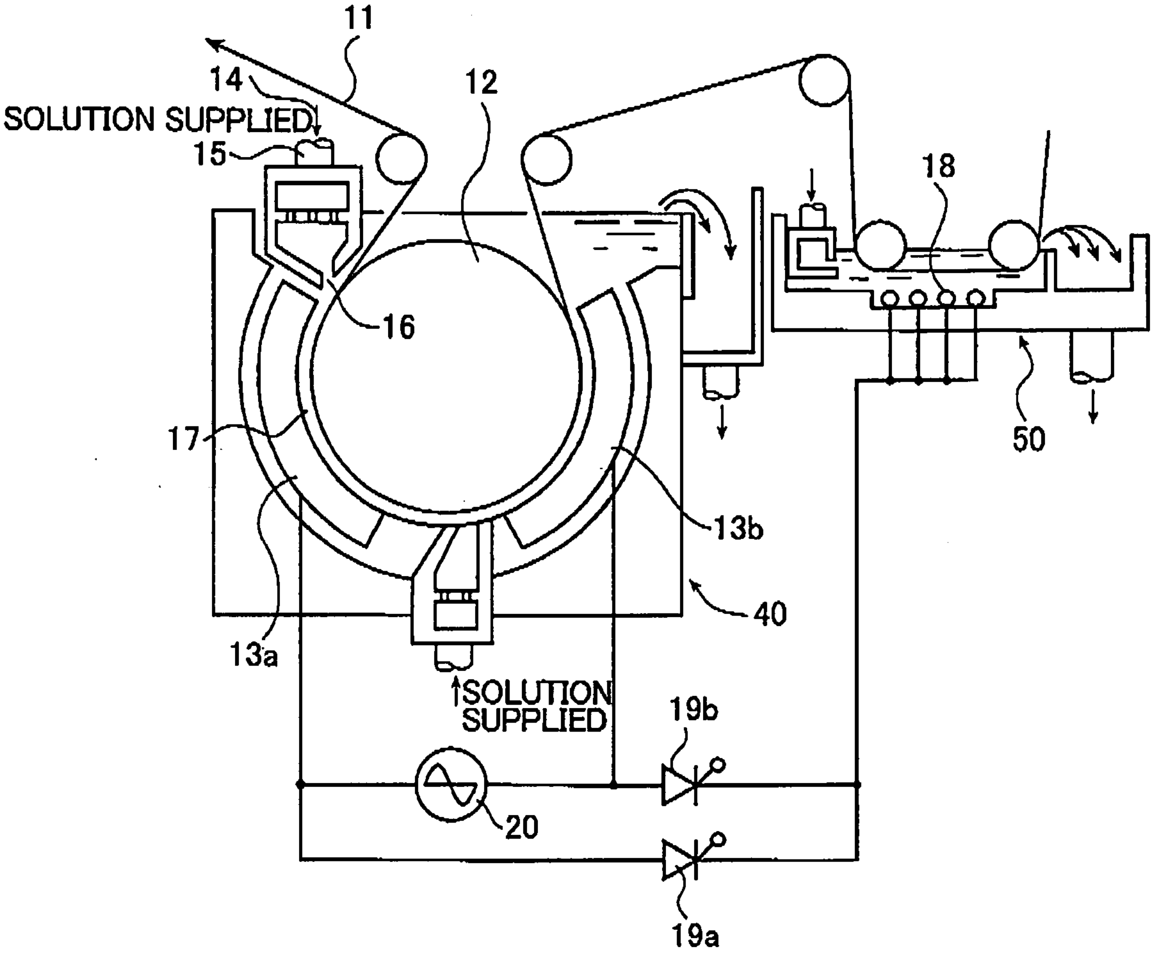

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FIG.5

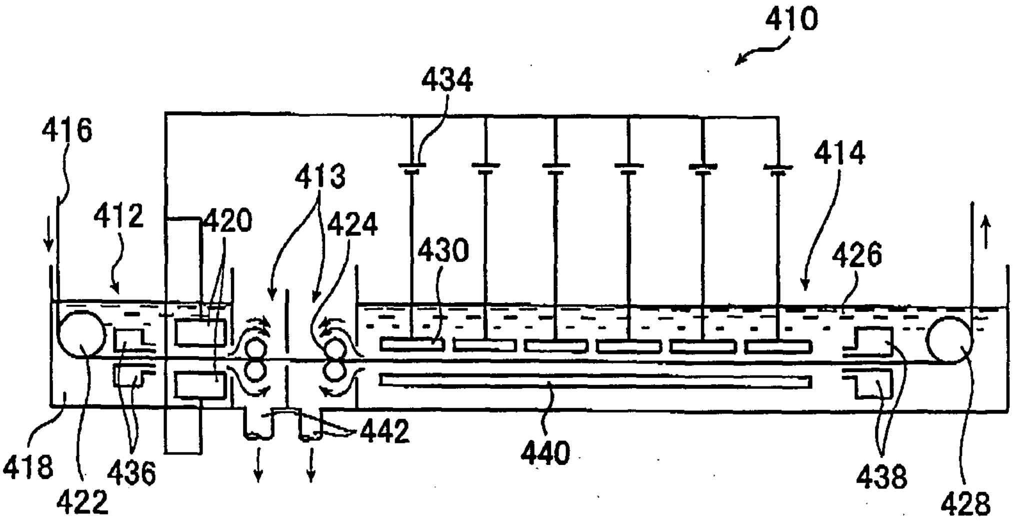
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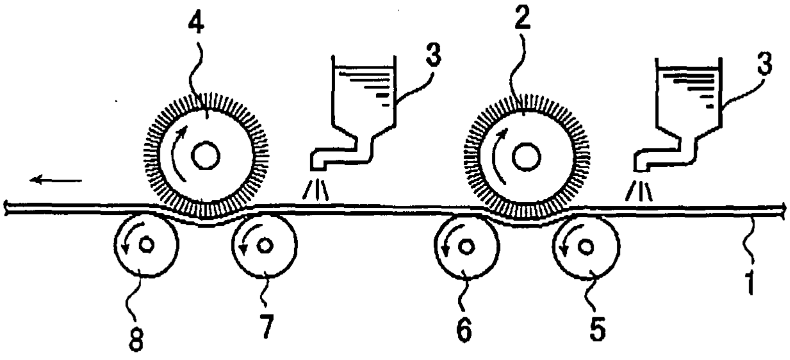
FIG.6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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 01 7672

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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
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L : document cited for other reasons
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