



US 20060032760A1

(19) **United States**(12) **Patent Application Publication****Nishino et al.**(10) **Pub. No.: US 2006/0032760 A1**(43) **Pub. Date: Feb. 16, 2006**(54) **METHOD OF MANUFACTURING
LITHOGRAPHIC PRINTING PLATE
SUPPORT****Publication Classification**(51) **Int. Cl.****C25D 5/18** (2006.01)**C25D 11/04** (2006.01)(52) **U.S. Cl.** **205/324; 205/102**(75) Inventors: **Atsuo Nishino**, Shizuoka (JP);
Hirokazu Sawada, Shizuoka (JP); **Akio**
Uesugi, Shizuoka (JP)

Correspondence Address:

SUGHRUE MION, PLLC**2100 PENNSYLVANIA AVENUE, N.W.****SUITE 800****WASHINGTON, DC 20037 (US)**(73) Assignee: **FUJI PHOTO FILM CO., LTD.**(21) Appl. No.: **11/203,214**(22) Filed: **Aug. 15, 2005**(30) **Foreign Application Priority Data**

Aug. 13, 2004 (JP) 2004-236002

(57)

ABSTRACT

Disclosed is a method of manufacturing a lithographic printing plate support having the step of: subjecting an aluminum plate at least to a first electrochemical graining treatment in which a first alternating current is passed through the aluminum plate in a first aqueous solution containing hydrochloric acid and nitric acid and a second electrochemical graining treatment in which a second alternating current is passed through the aluminum plate in a second aqueous solution containing hydrochloric acid in this order to obtain the lithographic printing plate support. By this method, a presensitized plate having excellent scumming resistance and a long press life is obtained.

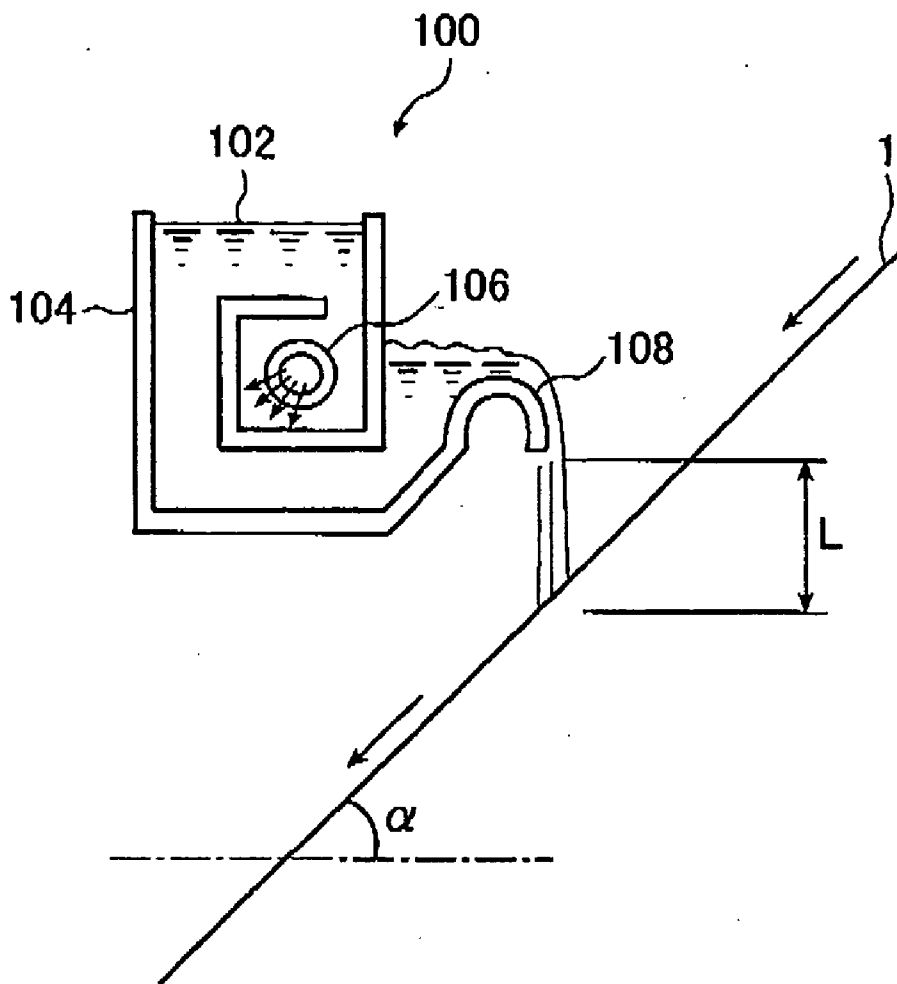


FIG. 3

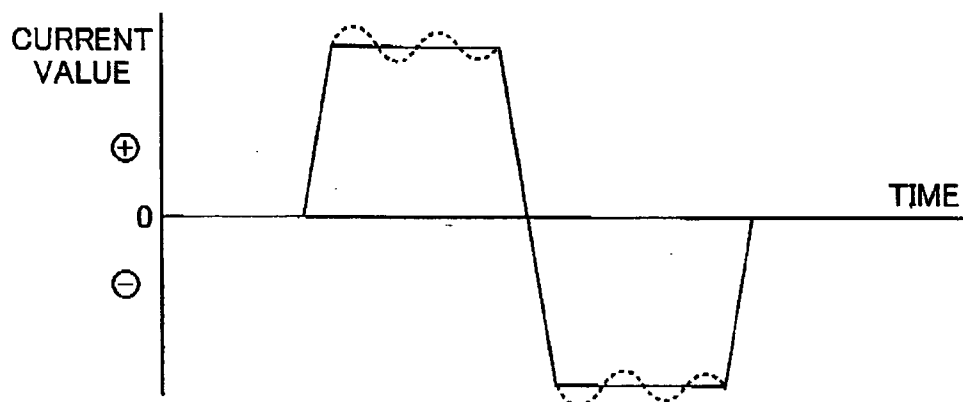


FIG. 4

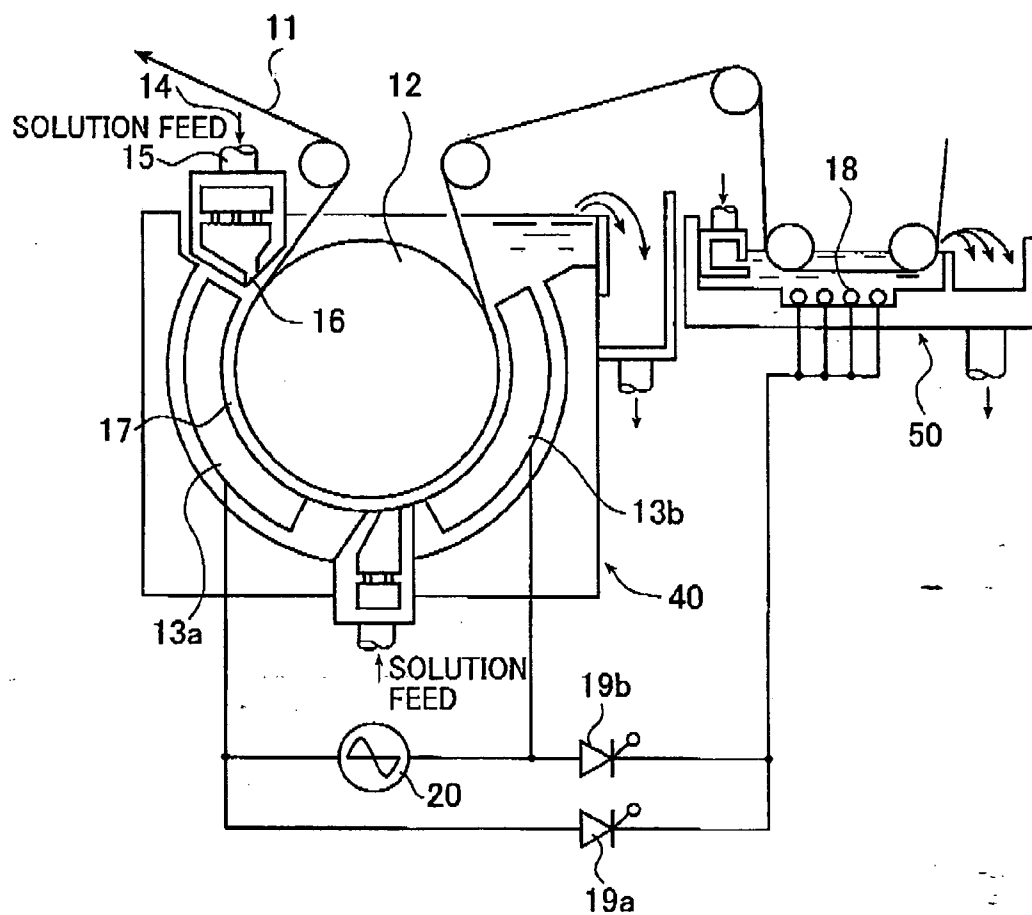


FIG. 5

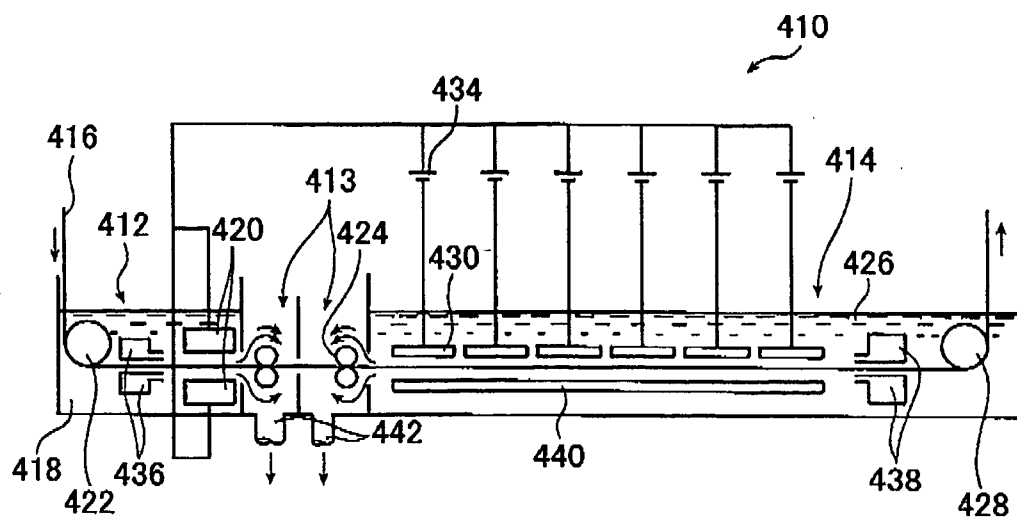
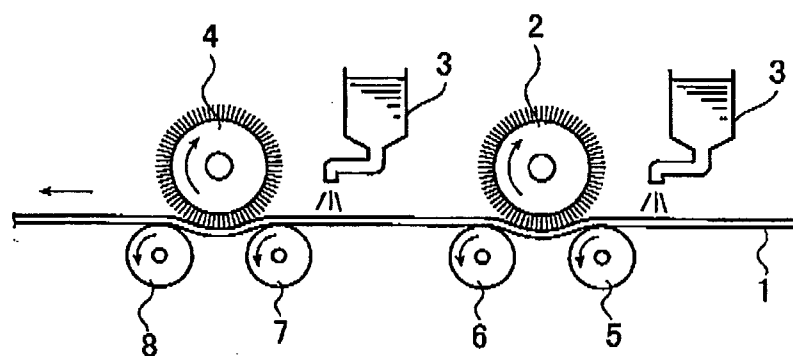


FIG. 6



METHOD OF MANUFACTURING LITHOGRAPHIC PRINTING PLATE SUPPORT

[0001] The entire contents of literatures cited in this specification are incorporated 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 that is used for a presensitized plate having excellent scumming resistance and a long press life.

[0003] An aluminum support for a lithographic printing plate that is used for a lithographic printing plate (hereinafter simply referred to as a "lithographic printing plate support") is manufactured by subjecting an aluminum plate to graining treatment and other surface treatments. Well known methods for the graining treatment include, for example, mechanical graining treatment, electrochemical graining treatment, chemical graining treatment (chemical etching) and a combination thereof.

[0004] Among these, the method in which an alternating current is passed through an aluminum plate in an aqueous solution containing hydrochloric acid is widely used in the electrochemical graining treatment, because fine asperities can be formed on the surface of the aluminum plate.

[0005] For example, 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/dm², 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 5 μ .

[0006] JP 51-6571 B describes a method of electrolyzing an aluminum sheet for a printing plate in which the aluminum sheet is continuously electrolyzed using an alternating current in an electrolyte solution containing 1 to 4 wt % of hydrochloric acid and 0.1 to 1 wt % of sulfuric acid.

[0007] JP 53-129132 A (the term "JP XX-XXXXXX A" as used herein means an "unexamined published Japanese patent application") describes a method of electrolytically graining an aluminum sheet in which the aluminum sheet is immersed in an aqueous electrolyte solution containing 1 wt % of hydrochloric acid and 4 to 6 wt % of nitric acid as the electrolyte, and an alternating current of 150 to 300 A/929 cm² (1 square foot) is applied to the aqueous electrolyte solution while maintaining the solution at a temperature of not less than 40° C.

[0008] JP 55-31199 B describes a method of graining an aluminum plate for use as a printing plate in which the aluminum plate whose surface was cleaned according to a conventional procedure is subjected to an alternating current electrolysis at a current density of 40 to 150 A/dm² in an electrolytic bath containing 0.5 to 2.5% of nitric acid and not more than 0.2% of hydrochloric acid.

[0009] JP 55-17579 A describes a method of manufacturing a printing plate support in which an aluminum plate is etched by alternating current electrolysis in an aqueous electrolyte solution containing (a) hydrogen chloride or nitric acid and (b) phosphoric acid or a salt thereof.

[0010] JP 56-101896 A describes a method of manufacturing a lithographic printing plate support in which the surface of an aluminum or aluminum alloy plate is subjected to an electrolytic etching in an electrolyte solution containing hydrochloric acid, nitric acid or a mixture acid thereof, then the aluminum or aluminum alloy plate is anodized in an electrolyte solution containing nitric acid, and the surface of the anodized plate is further subjected to mechanical polishing.

SUMMARY OF THE INVENTION

[0011] However, a lithographic printing plate manufactured using a lithographic printing plate support obtained by performing graining treatment according to the above-mentioned conventional method which uses the alternating current electrolysis in an aqueous solution containing hydrochloric acid had difficulty in fully satisfying both the properties of press life and scumming resistance.

[0012] Therefore, an object of the present invention is to provide a method of manufacturing a lithographic printing plate support that is capable of obtaining a presensitized plate having excellent scumming resistance and a long press life using the alternating current electrolysis in an aqueous solution containing hydrochloric acid.

[0013] The inventors of the present invention has made intensive studies to achieve the above object and as a result found that when an aluminum plate is subjected at least to a first electrochemical graining treatment in which an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid and nitric acid and a second electrochemical graining treatment in which an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid in this order to obtain a lithographic printing plate support, a presensitized plate using the support has both a long press life and excellent scumming resistance. The present invention has been completed based on the finding.

[0014] Accordingly, the present invention provides the following aspects (1) to (5):

[0015] (1) A method of manufacturing a lithographic printing plate support comprising the step of:

[0016] subjecting an aluminum plate at least to a first electrochemical graining treatment in which a first alternating current is passed through the aluminum plate in a first aqueous solution containing hydrochloric acid and nitric acid and a second electrochemical graining treatment in which a second alternating current is passed through the aluminum plate in a second aqueous solution containing hydrochloric acid in this order to obtain the lithographic printing plate support.

[0017] (2) The method according to (1), wherein the aluminum plate has a pattern of recessed and protruded portions on a surface thereof.

[0018] (3) The method according to (1) or (2), wherein the first alternating current is passed through the aluminum plate

in the first electrochemical graining treatment so that a total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm².

[0019] (4) The method according to any one of (1) to (3), wherein the second alternating current is passed through the aluminum plate in the second electrochemical graining treatment so that a total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm².

[0020] (5) The method according to any one of (1) to (4), wherein the first aqueous solution used in the first electrochemical graining treatment has a hydrochloric acid concentration of 3 to 30 g/L and a nitric acid concentration of 0.5 to 15 g/L.

[0021] As will be described later, the present invention can provide a lithographic printing plate support used for a presensitized plate which has excellent scumming resistance and a long press life when processed into a lithographic printing plate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] In the accompanying drawings:

[0023] FIG. 1 is a schematic cross-sectional view of an apparatus which carries out 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;

[0024] FIG. 2 is a conceptual view showing an exemplary electrolyte solution controlling method used in the method of manufacturing a lithographic printing plate support according to the present invention;

[0025] 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;

[0026] 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;

[0027] 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

[0028] 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

[0029] The present invention will be described below in detail.

Method of Manufacturing Lithographic Printing Plate Support Aluminum Plate (Rolled Aluminum)

[0030] 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.

[0031] In the present specification, the various above-described supports made of aluminum or aluminum alloy 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 %.

[0032] Aluminum plates that are suitable for use in the present invention are not specified here as to composition, but include known materials that appear in the 4th edition of Aluminum Handbook published in 1990 by the Japan Light Metal Association, such as aluminum plates having the designations JIS A1050, JIS A1100 and JIS A1070, and manganese-containing aluminum-manganese-based aluminum plates having the designation JIS A3004 and International Alloy Designation 3103A. To increase the tensile strength, it is preferable to use aluminum-magnesium alloys and aluminum-manganese-magnesium alloys (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 additionally contain zirconium and silicon, respectively may also be used. Use can also be made of aluminum-magnesium-silicon alloys.

[0033] 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.

[0034] 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.

[0035] The present applicant has disclosed related art concerning JIS 1050 materials in JP 59-153861 A, 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 3-2345.94 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.

[0036] 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.

[0037] 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, JP 6-37116 B, JP 2-215599 A and JP 61-201747 A.

[0038] This applicant has disclosed related art concerning aluminum-manganese alloys in JP 60-230951 A, JP 1-306288 A, JP 2-293189 A, JP 54-42284 B, JP 4-19290 B, 4-19291 B, JP 4-19292 B, JP 61-35995 A, JP 64-51992 A, JP 4-226394 A, U.S. Pat. No. 5,009,722 and U.S. Pat. No. 5,028,276.

[0039] The present applicant has disclosed related art concerning aluminum-manganese-magnesium alloys in JP 62-86143 A, JP 3-222796 A, JP 63-60824 B, JP 60-63346 A, JP 60-63347 A, JP 1-293350 A, EP 223,737, U.S. Pat. No. 4,818,300 and GB 1,222,777.

[0040] Also, this applicant has disclosed related art concerning aluminum-zirconium alloys in JP 63-15978 B, JP 61-51395 A, JP 63-143234 A and JP 63-143235 A.

[0041] This applicant has disclosed related art concerning aluminum-magnesium-silicon alloys in GB 1,421,710.

[0042] The aluminum alloy may be formed into a plate by a method such as the following, for example. First, an aluminum alloy melt that has been adjusted to a given alloying ingredient content is subjected to cleaning treatment by an ordinary method, 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.

[0043] 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 term "JP XX-XXXXXX U" as used herein means an "unexamined published Japanese utility model application"). The present applicant also discloses related art concerning the degassing of melts in JP 7-40017 A.

[0044] 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 moving mold, such as continuous casting.

[0045] In direct chill casting, the melt is solidified at a cooling speed of 0.5 to 30° C. per second. At less than 1° C., 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 cases 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.

[0046] 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 may 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.

[0047] 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 has been cut into discrete sheets. However, to enhance productivity, it is preferable to carry out such flattening with the rolled aluminum in the state of a continuous coil. 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 surface of 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.

[0048] 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, such as the Alusuisse Caster II mold, or a cooling block. When a continuous casting process is used, the melt is solidified at a cooling rate of 100 to 1,000° C./s. 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 by 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.

[0049] 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 a cooling belt (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 after casting, 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.

[0050] These continuously cast and rolled plates are then passed through such steps 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. 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.

[0051] The aluminum plate used in the present invention is well-tempered in accordance with H18 defined in JIS.

[0052] It is desirable for the aluminum plate manufactured as described above to have the following properties.

[0053] For the aluminum plate to achieve the stiffness required of a lithographic printing plate support, it should have a 0.2% offset yield strength of preferably at least 120 MPa. To ensure some degree of stiffness even when burning treatment has been carried out, the 0.2% offset yield 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 cases 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.

[0054] The aluminum plate more preferably has a tensile strength of 160 ± 15 N/mm², a 0.2% offset yield strength of 140 ± 15 MPa, and an elongation as specified in JIS Z2241 and Z2201 of 1 to 10%.

[0055] 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 μ m, more preferably up to 100 μ m, and most preferably up to 50 μ m. Moreover, the crystal structure has a length of preferably up to 5,000 μ m, more preferably up to 1,000 μ m, and most preferably up to 500 μ m. 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.

[0056] 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.

[0057] 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.

[0058] In the present invention, the aluminum plate as described above can be used after asperities are formed

thereon in the final rolling process or the like by press rolling, transfer or another method.

[0059] In particular, it is preferable to apply a method of forming a pattern of recessed and protruded portions on the surface of the aluminum plate by pressing a surface having a pattern of recessed and protruded portions onto the aluminum plate to transfer the pattern of recessed and protruded portions while performing cold rolling for adjusting the final plate thickness or finish cold rolling for finishing the surface shape after the final plate thickness is adjusted. More specifically, the method described in JP 6-262203 A can be advantageously used.

[0060] By use of the aluminum plate having the pattern of recessed and protruded portions on the surface, it is possible to obtain the pattern of recessed and protruded portions with uniform average pitches and depths as compared to a pattern of recessed and protruded portions formed by use of brushes and an abrasive. Moreover, it is possible to reduce energy consumption in subsequent alkaline etching treatment and surface roughening 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/m² 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 has a long press life.

[0061] It is particularly preferable to transfer onto the aluminum plate in the commonly performed final cold rolling process. The aluminum plate is preferably passed through rolls once to three times in rolling for transfer and the draft in each rolling process is preferably 3 to 8%.

[0062] Moreover, it is preferable to form the asperities on both surfaces of the aluminum plate by transfer. In this way, the stretch ratios on the front surface and the rear surface of the aluminum plate can be adjusted to approximately the same degree. Accordingly, it is possible to obtain the aluminum plate excellent in flatness.

[0063] Examples of the method of obtaining rolls for metal rolling that have asperities formed on the surfaces thereof and are used to transfer a pattern of recessed and protruded portions include blasting method, electrolytic method, laser method, electrical discharge machining method and a combination thereof. Among these, a method in which the blasting method is combined with the electrolytic method is preferable. Air blasting method is preferable as the blasting method.

[0064] The air pressure applied in the air blasting method is preferably 1 to 10 kgf/cm² (9.81×10^4 to 9.81×10^5 Pa) and more preferably 2 to 5 kgf/cm² (1.96×10^5 to 4.90×10^5 Pa).

[0065] There is no particular limitation on the grit used in the air blasting method as long as alumina particles each having a predetermined particle size are used. When alumina particles each having sharp edges are used for the grit, deep and uniform asperities can be easily formed on the surfaces of the transfer rolls.

[0066] The alumina particles have an average particle size of 50 to 150 μ m, preferably 60 to 130 μ m and more preferably 70 to 90 μ m. When the alumina particles fall within the above ranges, a sufficiently large surface rough-

ness for the transfer roll is obtained and hence the aluminum plate on the surface of which the asperities are formed using the transfer roll has a sufficiently large surface roughness. The number of pits formed can be also significantly increased.

[0067] It is preferable to carry out two to five blasts and more preferably two blasts in the air blasting method. When two blasts are carried out, the second blast is capable of scraping irregular projections off the asperities formed in the first blast. Therefore, locally deep recesses are hardly formed on the surface of the aluminum plate on which the asperities are formed using the thus obtained rolls for metal rolling. As a result, a lithographic printing plate obtained therefrom is excellent in developability (sensitivity).

[0068] The blast angle in the air-blasting method is preferably 60 to 120° and more preferably 80 to 100° with reference to the surface on which air is blasted (roll surface).

[0069] It is preferable that, after the air blasting treatment, but before the subsequently described plating treatment, the asperities formed by blasting be polished until the average surface roughness (R_a) is reduced by 10 to 40% from the value obtained after the air blasting. It is preferable to polish transfer rolls with sandpaper, a grindstone or a buff. Polishing allows the projections on the surface of the transfer roll to have even heights so that locally deep areas are not formed on the surface of an aluminum plate having asperities formed thereon using the transfer rolls. As a result, a lithographic printing plate obtained therefrom is excellent in developability (sensitivity).

[0070] 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 .

[0071] The number of peaks on the surface of the transfer roll is preferably 1,000 to 40,000/ mm^2 and more preferably 2,000 to 10,000/ mm^2 . When the number of peaks is too small, the water retention ability of the lithographic printing plate support and its adhesion to the image recording layer are impaired. The impaired water retention ability may cause scumming in the halftone dot areas when the support is formed into a lithographic printing plate.

[0072] There is no particular limitation on the material of the transfer roll and any known material for rolls for metal rolling can be used for example.

[0073] In the present invention, it is preferable to use steel rolls. Rolls fabricated by forging are particularly preferable. A preferable example of the composition of the 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.

[0074] Other examples of the steel that may generally be used in rolls for rolling metal 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. To achieve a long roll life, high-chromium alloy cast iron containing about 10 to 20 wt % of chromium may be used.

[0075] It is particularly preferable to use a roll fabricated by forging. 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.

[0076] The roll has preferably a diameter of 200 to 1,000 mm. The roll has preferably a circumferential length of 100 to 4,000 mm.

[0077] The transfer roll having asperities formed on the surface thereof by the air blasting method or the like is preferably subjected to a hardening treatment such as quenching or hard chromium plating after the transfer roll is rinsed, which enhances the wear resistance and prolongs the service life of the transfer roll.

[0078] The hard chromium plating is a particularly preferable hardening treatment. An electroplating method using a CrO_3 — SO_4 bath, a CrO_3 — SO_4 —fluoride bath or the like that is a conventionally known industrial chromium plating method can be used for the hard chromium plating.

[0079] 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 also significantly enhanced. The thickness of the layer formed by the hard chromium plating can be controlled through adjustment of the time for plating.

[0080] Before the roll is subjected to the hard chromium plating, the roll as an anode is preferably subjected to electrolytic treatment in a plating solution for use in the hard chromium plating, using a direct current with electricity in the range of 5,000 to 50,000 C/ dm^2 . The surface of the roll can have thus uniform asperities.

[0081] The average roughness R_a on the surface of the aluminum plate can be measured as follows: Two-dimensional roughness measurement is conducted by use of a stylus instrument for measuring surface roughness (such as "surfcom 575" made by Tokyo Seimitsu Co. Ltd.), and the average roughness R_a is measured five times according to ISO 4287 and an average value of the measurements is defined as the average roughness.

[0082] The conditions of the two-dimensional roughness measurement are described below.

Measurement Conditions

[0083] Cutoff value, 0.8 mm; slope correction, FLAT-ML; measurement length, 3 mm; vertical magnification, 10,000 $\times$; scan rate, 0.3 mm/s; stylus tip diameter, 2 μm .

[0084] R_{max} and R_{sm} can be measured according to ISO 4287.

[0085] The aluminum plate used in this invention is in the form of a continuous strip or discrete sheets. That is, it may be either an aluminum web or individual sheets cut to a size which corresponds to the presensitized plates that will be shipped as the final product.

[0086] 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 forming 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.

[0087] 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 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.

[0088] 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

[0089] In the method of manufacturing a lithographic printing plate support according to the present invention, the aluminum plate described above is subjected at least to an electrochemical graining treatment (hereinafter referred to as a "first electrochemical graining treatment") in which an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid and nitric acid (the solution being hereinafter referred to as a "first electrolyte") and another electrochemical graining treatment (hereinafter referred to as a "second electrochemical treatment") in which an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid (the solution being hereinafter referred to as a "second electrolyte") in this order to obtain a lithographic printing plate support.

[0090] The method of manufacturing a lithographic printing plate support in the present invention may also include various other processes than the above treatments.

[0091] More specifically, a 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"), first 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"), second electrochemical graining treatment, etching treatment in an aqueous alkali solution (hereinafter referred to as "third etching treatment"), desmutting treatment in an aqueous acidic solution (hereinafter referred to as "third desmutting treatment"), and anodizing treatment are carried out in this order can be preferably used.

[0092] Another method in which sealing treatment or hydrophilizing treatment or both are carried out after the anodizing treatment is also preferable.

[0093] It is also possible to perform mechanical graining treatment before the first etching treatment. The amount of electricity used in the first electrochemical graining treatment can be thus reduced.

[0094] 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.

[0095] A transfer method in which a surface with asperities is pressed onto an aluminum plate (transfer roll method) can be also employed. That is, applicable methods include those described in JP 55-74898-A, JP 60-36195 A, JP 60-203496 A, as well as a method described in JP 6-55871 A characterized in that transfer is repeated several times, and a method described in JP 6-b24168 A characterized in that the surface is elastic.

[0096] 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 finish cold rolling for finishing the surface shape after the final plate thickness is adjusted.

[0097] The respective surface treatment processes will be described below in detail.

First Etching Treatment

[0098] 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.

[0099] The purpose of the first etching treatment carried out prior to the first electrochemical graining treatment is to enable the formation of uniform recesses in the first electrochemical graining treatment and to remove substances such as rolling oil, contaminants and a naturally oxidized film from the surface of the aluminum plate (rolled aluminum).

[0100] In the first etching treatment, the amount of material removed by etching (also referred to below as the "etching amount") from the surface to be subsequently subjected to the electrochemical graining treatment is preferably at least 0.5 g/m², more preferably at least 1 g/m², but preferably not more than 10 g/m², more preferably not more than 5 g/m². In the etching amount of 0.5 g/m² or more, uniform pits can be formed in the subsequent first electrochemical graining treatment. In the etching amount of 10 g/m² or less, the amount of aqueous alkali solution used is decreased, which is economically advantageous.

[0101] The amount of the material removed by etching from the opposite side to the surface to be subsequently subjected to the electrochemical graining treatment is preferably at least 5%, more preferably at least 10%, but preferably not more than 50%, more preferably not more than 30% of the amount of the material removed from the surface to be subjected to the electrochemical graining treatment. When the amount of the material falls within the above ranges, a suitable balance can be struck between the removal effect of rolling oil from the rear side of the aluminum plate and the economical efficiency.

[0102] This is also the case with the second and third etching treatments to be described later.

[0103] 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 aldionates 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. Of these, 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.

[0104] 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 %.

[0105] 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.

[0106] 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.

[0107] 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.

[0108] When the aluminum plate is continuously etched, the aluminum ion concentration in the alkali solution rises and the amount of material etched from the aluminum plate changes. It is thus preferable to control the etching solution composition as follows.

[0109] 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 measured 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.

[0110] The conductivity meter and hydrometer used to measure electrical conductivity and specific gravity are each

preferably temperature-compensated instruments. The hydrometer is preferably a pressure differential hydrometer.

[0111] 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 a tank filled with an alkali solution, and a method in which the surface of the aluminum plate is sprayed with an alkali solution.

[0112] The most desirable of these is a method that involves spraying the surface of the aluminum plate with an alkali solution. A method in which the etching solution is sprayed onto the aluminum plate at a rate of 10 to 100 L/min per spray line from preferably a plurality of spray lines bearing 2 to 5 mm diameter openings at a pitch of 10 to 50 mm is especially desirable.

[0113] 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.

[0114] Rinsing treatment is preferably carried out by rinsing with a rinsing apparatus that uses a free-falling curtain of water and also by rinsing with spray lines.

[0115] FIG. 1 is a schematic cross-sectional view of an apparatus 100 which carries out rinsing with a free-falling curtain of water. As shown in FIG. 1, the apparatus 100 that carries out rinsing treatment 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.

[0116] In this apparatus 100, the pipe 106 feeds water 102 to the water holding tank 104. When the water 102 overflows from 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 over which the water 102 between the apparatus 100 and the aluminum plate 1 exists as a free-falling curtain of liquid 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°.

[0117] 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.

[0118] 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.

[0119] Alternatively, rinsing may be carried out with a spray line having a plurality of spray tips that discharge fan-like sprays of water and are disposed along the width of the aluminum plate. The interval between the 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

[0120] 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 an acidic solution into contact with the aluminum plate.

[0121] 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. More specifically, for example, wastewater from the aqueous sulfuric acid solution used in the anodizing treatment step to be described later, wastewater from the electrolyte solution used in the first electrochemical graining treatment or wastewater from the electrolyte solution used in the second electrochemical graining treatment can be preferably used.

[0122] The composition of the desmutting treatment solution can be controlled by selecting and using a method in which the electrical conductivity and temperature are controlled with respect to a matrix of the acidic solution concentration and the aluminum ion concentration, a method in which the electrical conductivity, specific gravity and temperature are instead controlled with respect to the above matrix, or a method in which the electrical conductivity, ultrasonic wave propagation velocity and temperature are instead controlled.

[0123] 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.

[0124] The temperature of the acidic solution is in the range of 25° C. to 95° C.

[0125] 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.

[0126] 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 a tank filled with the acidic solution, and spraying the acidic solution onto the surface of the aluminum plate.

[0127] Of these, a method in which the acidic solution is sprayed onto the surface of the aluminum plate is preferred. More specifically, a method in which a desmutting solution is sprayed from at least one spray line, and preferably two or more spray lines, each having 2 to 5 mm diameter openings spaced at a pitch of 10 to 50 mm, at a rate of 10 to 100 L/min per spray line is desirable.

[0128] After desmutting treatment, it is preferable to remove the solution with nip-rollers, then to carry out rinsing treatment with water for 1 to 10 seconds and again remove the water with nip rollers.

[0129] Rinsing treatment is the same as rinsing treatment following alkali etching treatment. However, it is preferable for the amount of water used per spray tip to be from 1 to 20 L/min.

First Electrochemical Graining Treatment

[0130] In the first electrochemical graining treatment, an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid and nitric acid (first electrolyte) for electrochemical graining treatment. The first electrochemical graining treatment is capable of obtaining the aluminum plate having a surface shape in which pits having an average diameter of 0.01 to 0.5 μm are superimposed on recesses (pits) having an average diameter of 1 to 5 μm , the pits are uniformly formed and there are a few plateau portions. Since the aluminum plate after the first electrochemical graining treatment has been carried out has recesses uniformly formed on the surface thereof, the lithographic printing plate obtained therefrom has a long press life. Further, since the pits are uniformly formed on the surface of the aluminum plate, the lithographic printing plate obtained therefrom has excellent scumming resistance.

[0131] When an alternating current is passed through the aluminum plate in an aqueous solution containing hydrochloric acid for electrochemical graining treatment, the shape of pits formed on the surface of the aluminum plate varies with the waveform of the alternating current used. On the other hand, when an alternating current is passed through the aluminum plate in an aqueous solution containing no hydrochloric acid but nitric acid for electrochemical graining treatment, the shape of pits formed on the surface of the aluminum plate does not vary with the waveform of the alternating current used. Since the first electrolyte contains hydrochloric acid in the present invention, the shape of the pits formed on the surface of the aluminum plate can be controlled in the first electrochemical graining treatment by changing the waveform of the alternating current.

[0132] When the first electrolyte contains no nitric acid, not pits having an average diameter of 1 to 5 μm but only pits having an average diameter of 0.01 to 0.5 μm are formed on the surface of the aluminum plate. Therefore, the aluminum plate obtained does not have the surface shape in which the pits having an average diameter of 0.01 to 0.5 μm are superimposed on the pits having an average diameter of 1 to 5 μm .

[0133] The concentration of hydrochloric acid in the first electrolyte is preferably 3 to 30 g/L, more preferably 4 to 20 g/L and even more preferably 10 to 18 g/L. When the concentration falls within the above ranges, uniformity of the pits formed is enhanced.

[0134] The concentration of nitric acid in the first electrolyte is preferably 0.5 to 15 g/L and more preferably 1 to 10 g/L. The nitric acid may be added in the form of a nitrate compound such as aluminum nitrate, sodium nitrate or ammonium nitrate.

[0135] The first electrolyte used may also contain sulfuric acid.

[0136] Instead of sulfuric acid, the first electrolyte used may also contain a chloride compound containing a chloride ion such as aluminum chloride, sodium chloride or ammonium chloride or a sulfate compound containing a sulfate ion such as aluminum sulfate, sodium sulfate or ammonium sulfate.

[0137] 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 metals which are present in the aluminum alloy, such as iron, copper, manganese, nickel, titanium, magnesium and silicon. Hypochlorous acid and hydrogen peroxide may be added in an amount of 1 to 100 g/L.

[0138] The first electrolyte has preferably an aluminum ion concentration of 3 to 30 g/L, more preferably 3 to 20 g/L and even more preferably 8 to 18 g/L. When the aluminum ion concentration falls within the above ranges, uniformity of the pits formed is enhanced. The replenishment amount of the first electrolyte is not increased too much. It is particularly preferred to adjust the aluminum ion concentration in the electrolyte solution using aluminum chloride.

[0139] It is preferable to perform concentration control of each component of the first electrolyte using a concentration measuring method such as a multi-component concentration measuring method in combination with feedforward control and feedback control. This makes it possible to correctly control the concentration of the first electrolyte used for the electrolyte solution.

[0140] 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 first electrolyte and the electrical conductivity of the electrolyte, neutralization titration, capillary electrophoretic analysis, isotachophoretic analysis and ion chromatography.

[0141] Depending on the type of a detector used, the ion chromatography is classified into ion chromatography for absorbance detection, non-suppressor type ion chromatography for conductivity detection and suppressor type ion chromatography. Among these, the suppressor type ion chromatography is preferable because the measurement stability is ensured.

[0142] More specifically, it is preferable to control the concentration of each component of the electrolyte solution by the method described below.

[0143] In the electrochemical graining treatment, the hydrogen ion concentration of the electrolyte solution is decreased and the aluminum ion concentration thereof is increased in accordance with the amount of applied electricity. Therefore, the feedforward control based on the amount of applied electricity allows the hydrogen ion concentration and the aluminum ion concentration to be kept constant.

[0144] In other words, an acid is added to the electrolyte solution in an amount corresponding to the amount of electricity, that is, the value of a current generated in the AC power source to thereby increase the hydrogen ion concentration, water is added to the electrolyte solution in an amount corresponding to the amount of electricity to thereby decrease the aluminum ion concentration, and the acid is further added to the electrolyte solution in an amount corresponding to the amount of water added to compensate for the decrease of the acid concentration due to the addition of water, whereby the hydrogen ion concentration and the aluminum ion concentration can be kept constant. In the following description, water added to the electrolyte solution is also referred to as "replenishment water".

[0145] It is further preferable to control the concentration of each component of the electrolyte solution by providing

a concentration measuring system for measuring the concentration of each component of the electrolyte solution, and using in combination the feedback control in which the supply of the acid and replenishment water is controlled based on the measured component concentration of the electrolyte solution. The use of the feedback control allows the concentration of each component of the electrolyte solution to be controlled with high accuracy even in the case where the electrolyte solution of the previous step is taken in this step with the aluminum plate, the electrolyte solution in this step is taken out with the aluminum plate, or the electrolyte solution evaporates.

[0146] An example of the concentration measuring method is the multi-component concentration measuring method mentioned above. Particularly preferred is a method in which the relation between the electrical conductivity of the electrolyte solution and the ultrasonic wave propagation velocity in accordance with the compositional ratio of the respective components in the solution is established in advance and the concentration measurement is carried out based on the values of the electrical conductivity and ultrasonic wave propagation velocity.

[0147] The replenishment water and the acid are preferably supplied to a circulation tank, which stores the electrolyte solution. The electrolyte solution stored in the circulation tank is supplied to an electrolytic cell and the electrolyte solution discharged from the electrolytic cell is returned to the circulation tank. When exceeding the capacity of the circulation tank, the electrolyte solution overflows and is discharged as wastewater to a river or the like after having been made harmless.

[0148] The present invention performs concentration control for three components of hydrochloric acid, nitric acid and aluminum ion, but it is difficult to measure the concentrations of the three components in real time. Therefore, it is preferable to use a method in which nitric acid is added in advance to the replenishment water in the same concentration as that of nitric acid in the electrolyte solution and the replenishment water including the nitric acid added thereto and hydrochloric acid are added to the electrolyte solution to thereby control the concentrations.

[0149] In this method, it is preferable to control the nitric acid concentration in the replenishment water as well. An example of the method of controlling the nitric acid concentration in the replenishment water is a method in which nitric acid or water is added to the replenishment water based on the result obtained by measuring the concentration of nitric acid in the replenishment water. Examples of the method of measuring the nitric acid concentration in the replenishment water include a method in which the concentration is measured based on the electrical conductivity, pH or specific gravity of the replenishment water, or ultrasonic wave propagation velocity in the replenishment water, neutralization titration, capillary electrophoretic analysis, isotachophoretic analysis and ion chromatography. A measuring method using the electrical conductivity of the replenishment water is preferably used.

[0150] FIG. 2 is a conceptual view showing an example of a system for controlling the concentration of the electrolyte solution (hereinafter referred to as a "concentration control system") in the present invention.

[0151] Referring to FIG. 2, a current is output from an AC power source 201 to electrodes 202, whereby the first

electrochemical graining treatment is carried out on an aluminum plate **204** that passes through an electrolyte solution **220** stored in an electrolytic cell **203**. A concentration control system **200** controls the concentrations of the components of the electrolyte solution **220** in the electrolytic cell **203**.

[0152] The concentration control system **200** includes a circulation tank **210**, a first concentration measuring system **211** that measures the concentrations of hydrochloric acid **221** and aluminum ions in the electrolyte solution **220** stored in the circulation tank **210**, a hydrochloric acid tank **212** that stores hydrochloric acid **221**, a replenishment water tank **213** that stores replenishment water **222** containing water and nitric acid, a controller **214** that controls the supply of the hydrochloric acid **221** and/or the replenishment water **222** to the circulation tank **210** based on data provided from the AC power source **201** and the first concentration measuring system **211**, and a second concentration measuring system **215** that measures the concentration of the nitric acid in the replenishment water **222**. In FIG. 2, reference symbol P denotes a pump, solid lines indicate liquid movements, and broken lines indicate signal flows.

[0153] In the concentration control system **200**, the first concentration measuring system **211** measures the concentrations of hydrochloric acid and aluminum ions in the electrolyte solution **220** stored in the circulation tank **210** and the controller **214** controls the supply of hydrochloric acid from the hydrochloric acid tank **212** to the circulation tank **210** and the supply of replenishment water from the replenishment water tank **213** to the circulation tank **210** based on the concentrations measured by the first concentration measuring system **211** and a current generated in the AC power source **201**, whereby the concentration control is carried out. The electrolyte solution **220** stored in the circulation tank **210** is supplied to the electrolytic cell **203** and the electrolyte solution **220** discharged from the electrolytic cell **203** is returned to the circulation tank **210**.

[0154] In the concentration control system **200**, the concentration of nitric acid in the replenishment water **222** stored in the replenishment water tank **213** is measured by the second concentration measuring system **215** and water and/or nitric acid is supplied to the replenishment water tank **213** based on the measurement result, whereby the concentration control is carried out.

[0155] To add to the electrolyte solution, 10 to 35 wt % of hydrochloric acid is preferably used.

[0156] Further, it is preferable to use 10 to 68 wt % of nitric acid to add to the replenishment water so that the nitric acid in the replenishment water can have a desired concentration.

[0157] It is also preferable for the nitric acid in the replenishment water to have the same concentration as that desired in the electrolyte solution. In other word, when the electrolyte solution has a nitric acid concentration of, for example, 5 g/L, the replenishment water should also have a nitric acid concentration of 5 g/L. If the replenishment water and the electrolyte solution are identical in the nitric acid concentration, the nitric acid concentration in the electrolyte solution can be kept substantially constant without measurement thereof.

[0158] The temperature of the first electrolyte 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.

[0159] The first 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. Special waveforms described in JP 52-58602 A may also be used. Use can also be made of the waveforms described in JP 3-79799 A. Other processes that may be employed for this purpose include those described in JP 55-158298 A, JP 56-28898 A, JP 52-58602 A, JP 52-152302 A, JP 54-85802 A, JP 60-190392 A, JP 58-120531 A, JP 63-176187 A, JP 1-5889 A, JP 1-280590 A, JP 1-118489 A, JP 1-148592 A, JP 1-178496 A, JP 1-188315 A, JP 1-154797 A, JP 2-235794 A, JP 3-260100 A, JP 3-253600 A, JP 4-72079 A, JP 4-72098 A, JP 3-267400 A and JP 1-141094 A. In addition to the above, electrolytic treatment can also be carried out using alternating currents of special frequency such as have been proposed in connection with methods for manufacturing electrolytic capacitors. These are described in, for example, U.S. Pat. No. 4,276,129 and U.S. Pat. No. 4,676,879.

[0160] Various electrolytic cells and power supplies have been proposed for use in electrolytic treatment. For example, use may be made of those described in U.S. Pat. No. 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.

[0161] Further, uniform graining of an aluminum plate containing a large amount of Cu is made possible by adding and using a compound which may form a complex with Cu. Examples of the compound which may form a complex with Cu include ammonia; amines obtained by substituting a hydrogen atom of the ammonia with an (aliphatic or aromatic) hydrocarbon group or the like as exemplified by methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine, cyclohexylamine, triethanolamine, triisopropanolamine and EDTA (ethylenediaminetetraacetic acid); and metal carbonates such as sodium carbonate, potassium carbonate and potassium hydrogencarbonate. Ammonium salts such as ammonium nitrate, ammonium chloride, ammonium sulfate, ammonium phosphate and ammonium carbonate are also included.

[0162] No particular limitation is imposed on the alternating current waveform used in the first electrochemical graining treatment. For example, a sinusoidal, square, trapezoidal or triangular waveform may be used but a trapezoidal or sinusoidal waveform is preferred and a sinusoidal waveform is more preferred.

[0163] "Trapezoidal waveform" refers herein to a waveform like that shown in FIG. 3. In the trapezoidal waveform,

it is preferable for the time until the current reaches a peak from zero (current rise time) to be 0.5 to 3.5 msec and more preferably 0.8 to 2.5 msec. When the time is at least 0.5 msec, the cost required for producing a power supply is decreased. When the time is not more than 3.5 msec, more uniform pits are obtained.

[0164] The current rise time can be arbitrarily selected when a triangular waveform is used.

[0165] When a sinusoidal waveform is used, a commercial alternating current or other current which has substantially a sinusoidal waveform can be used without any particular limitation.

[0166] The alternating current has preferably a duty ratio of 0.33 to 0.66 and more preferably 0.45 to 0.55. The duty ratio is a value obtained by dividing the anodic reaction time of the aluminum plate in one cycle by the time of one cycle.

[0167] The alternating current used in the first electrochemical graining treatment has preferably a frequency in the range of 10 to 200 Hz, more preferably 20 to 150 Hz and even more preferably 30 to 120 Hz. When the frequency is 10 Hz or more, facet-shaped (sugarish) large pits are not easily formed and more excellent scumming resistance is achieved. When the frequency is not more than 200 Hz, the current condition is not susceptible to inductance components on a power circuit through which an electrolytic current passes and a high-capacity power supply can be easily produced.

[0168] The amount of electricity in the first electrochemical graining treatment is preferably in the range of 100 to 300 C/dm² in terms of the total amount of electricity when the aluminum plate serves as an anode. When the amount of electricity is at least 100 C/dm², a sufficient surface roughness and a longer press life are obtained and the amount of water during printing can be more easily adjusted. When the amount of electricity is not more than 300 C/dm², markedly profound recesses cannot be easily formed and hence a lithographic printing plate support having more excellent scumming resistance is obtained.

[0169] The current density in the first electrochemical graining treatment at the peak current value is preferably 10 to 300 A/dm², more preferably 15 to 200 A/dm² and even more preferably 20 to 125 A/dm². When the current density is at least 10 A/dm², the productivity is further enhanced. When the current density is not more than 300 A/dm², the voltage is not so high and the capacity of the power supply is not increased too much, which allows the cost of the power supply to be decreased.

[0170] For example, a power supply using a commercial alternating current or an inverter-controlled power supply can be used for the power supply. Among these, an inverter-controlled power supply using an IGBT (Insulated Gate Bipolar Transistor) is preferable because any waveform can be generated by the PWM (Pulse Width Modulation) control and this power supply is excellent in the tracking capability when the current value (current density of the aluminum plate) is kept constant by changing the voltage with respect to the changes of the width and thickness of the aluminum plate and the concentration of each component in the electrolyte solution.

[0171] FIG. 4 is a side view of a radial electrolytic cell that is used to carry out electrochemical graining treatment

using alternating current in the method of manufacturing a lithographic printing plate support according to the present invention.

[0172] One or more AC power supply 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 furnished for the anodic reaction which acts on the aluminum plate opposite the main electrodes and the current value furnished for the cathodic reaction. The current ratio QR/QF (ratio between the total amount of electricity QR when the aluminum plate serves as a cathode and the total amount of electricity QF when the aluminum plate serves as an anode) in the main electrolytic cell is preferably 0.9 to 3 and more preferably 0.9 to 1.0.

[0173] Any known electrolytic cell employed for surface treatment, including vertical, flat and radial type electrolytic cells, may be used to carry-out electrochemical graining treatment in the method of manufacturing a lithographic printing plate support. Radial-type electrolytic cells such as those described in JP 5-195300 A are especially preferred in that pits are prevented from being formed on the rear surface of an aluminum plate in the electrochemical graining treatment. When using a flat type electrolytic cell, it is preferable to adopt a method in which an insulating plate is provided on a non-treated surface of an aluminum plate to prevent a current from passing over the non-treated surface to thereby prevent pit formation on the non-treated rear surface of the aluminum plate in the electrochemical graining treatment. The electrolyte solution is passed through the electrolytic cell either parallel or counter to the direction in which the aluminum web advances.

[0174] The electrolytic cell may be divided into sections. In this case, the electrolytic conditions of each section of the electrolytic cell may be the same or different.

[0175] Following completion of the first 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.

[0176] 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, each of which discharges a fan-like spray of water and is situated along the width of the aluminum plate. 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. Rinsing with a plurality of spray lines is preferred.

Second Etching Treatment

[0177] The purpose of the second etching treatment carried out between the first electrochemical graining treatment and the second electrochemical graining treatment is to dissolve smut that arises in the first electrochemical graining treatment and to dissolve the edges of the pits formed by the first electrochemical graining treatment. The present step dissolves the edges of the large pits formed by the first 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.

[0178] 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 20 to 40 wt % of alkali solution containing 4 to 8 wt % of aluminum ions or 4 to 6 wt % of 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.

[0179] The etching amount is preferably at least 0.01 g/m², and more preferably at least 0.1 g/m², but preferably not more than 6 g/m², more preferably not more than 3 g/m², and even more preferably not more than 1.5 g/m².

Second Desmutting Treatment

[0180] 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 be carried out in the same way as the first desmutting treatment.

Second Electrochemical Graining Treatment

[0181] In the second electrochemical graining treatment, the aluminum plate is subjected to electrochemical graining treatment with alternating current in an aqueous solution containing hydrochloric acid (second electrolyte). Fine pits having an average aperture diameter of 0.01 to 0.5 μ m are uniformly formed on the entire surface of the aluminum plate by carrying out the second electrochemical graining treatment. Particularly in the case where the second etching treatment described above is carried out, sharply contoured fine pits having an average aperture diameter of 0.01 to 0.5 μ m are deeply formed on the surface smoothed as a result of the dissolution of the edges of the large pits in the second etching treatment. A significantly long press life is thus achieved.

[0182] The second electrochemical graining treatment is basically the same as the first electrochemical graining treatment except that the aqueous solution containing hydrochloric acid is used when the aluminum plate is subjected to the second electrochemical graining treatment. Different points from the first electrochemical graining treatment will be mainly described below.

[0183] The second electrolyte has preferably a hydrochloric acid concentration of 3 to 30 g/L, more preferably 5 to 20 g/L and even more preferably 5 to 15 g/L. When the concentration falls within the above ranges, uniformity of the pits formed is enhanced.

[0184] The second electrolyte may contain 0.5 to 10 g/L of sulfuric acid or nitric acid. Sulfuric acid and nitric acid form

an oxide film through an anodic reaction. The surface having deeper, finer and more uniform asperities can be thus formed.

[0185] The second electrolyte has more preferably the same composition as that of the first electrolyte. In other words, the second electrolyte is more preferably the aqueous solution containing hydrochloric acid and nitric acid that was used in the first electrochemical graining treatment. The number of kinds of aqueous solutions used in the electrochemical graining treatments can be thus reduced.

[0186] In addition, when the first and second electrolytes are identical in the composition and the solution temperature, these electrolytes can be used in a single apparatus for controlling the concentration of the electrolyte solution and in a single circulation tank, which enables equipment cost reduction. Therefore, it makes it possible to reduce the cost required for graining of aluminum plates and to efficiently carry out the first and second electrochemical graining treatments on aluminum plates.

[0187] The aluminum ion concentration in the second electrolyte is preferably 3 to 30 g/L, more preferably 3 to 20 g/L and even more preferably 4 to 15 g/L. When the aluminum ion concentration falls within the above ranges, uniformity of the pits formed is enhanced and the replenishment amount of the second electrolyte is not increased too much. It is particularly preferred to adjust the aluminum ion concentration in the electrolyte solution using aluminum chloride.

[0188] No particular limitation is imposed on the AC power supply waveform used in the second electrochemical graining treatment. For example, a sinusoidal, square, trapezoidal or triangular waveform may be used but trapezoidal, sinusoidal or triangular waveform is preferable. When the trapezoidal waveform is used, it is preferable for the time until the current reaches a peak from zero to be 0.3 to 2.0 msec and more preferably 0.5 to 1.0 msec. When the time is at least 0.3 msec, the cost required for producing a power supply is decreased. When the time is not more than 2 msec, more uniform pits are obtained.

[0189] The current rise time can be arbitrarily selected when a triangular waveform is used.

[0190] The alternating current has preferably a duty ratio of 0.33 to 0.66 and more preferably 0.45 to 0.55.

[0191] The alternating current has preferably a frequency of 10 to 200 Hz, more preferably 20 to 150 Hz and even more preferably 40 to 120 Hz. When the frequency is 10 Hz or more, facet-shaped large pits are not easily formed and more excellent scumming resistance is achieved. When the frequency is not more than 200 Hz, the current condition is not susceptible to inductance components on a power circuit through which an electrolytic current passes and a high-capacity power supply can be easily produced.

[0192] The amount of electricity in the second electrochemical graining treatment is preferably in the range of 10 to 300 C/dm², more preferably 30 to 150 C/dm² and even more preferably 50 to 100 C/dm² in terms of the total amount of electricity when the aluminum plate serves as an anode. When the amount of electricity is at least 10 C/dm², a longer press life is achieved. When the amount of

electricity is not more than 300 C/dm², more excellent scumming resistance is achieved.

[0193] The current ratio is preferably 0.9 to 3.0, more preferably 0.95 to 2.0 and even more preferably 0.95 to 1.0.

Third Etching Treatment

[0194] The purpose of the third etching treatment carried out after the second electrochemical graining treatment is to dissolve smut that arises in the second electrochemical graining treatment and to dissolve the edges of the pits formed by the second electrochemical graining treatment.

[0195] The third etching treatment is basically the same as the first etching treatment. The etching amount is preferably at least 0.01 g/m², and more preferably at least 0.1 g/m², but preferably not more than 10 g/m², and more preferably not more than 3 g/m².

Third Desmutting Treatment

[0196] After the third etching treatment has been carried out, it is preferable to carry out acid pickling (third desmutting treatment) to remove contaminants (smut) remaining on the surface of the aluminum plate. The third desmutting treatment can be carried out basically in the same way as the first desmutting treatment.

[0197] When the same type of the electrolyte solution as that used in the subsequent anodizing treatment is used for the desmutting solution in the third desmutting treatment, solution removal with nip rollers and rinsing with water that are to be carried out after the desmutting treatment can be omitted.

[0198] The third desmutting treatment is preferably carried out in an electrolytic cell of an anodizing apparatus used in anodizing treatment to be described later where the aluminum plate is to be subjected to cathodic reaction. This configuration eliminates the necessity for providing an independent desmutting bath for the third desmutting treatment, which may lead to equipment cost reduction.

Anodizing Treatment

[0199] The aluminum plate treated as described above is also 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 surface of the aluminum plate by passing a current through the aluminum plate as the anode in, for example, a solution having a sulfuric acid concentration of 50 to 300 g/L and an aluminum ion concentration of up to 5 wt %. The solution used for anodizing treatment includes any one or combination of, for example, sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid and amidosulfonic acid.

[0200] It is acceptable for ingredients ordinarily present in at least the aluminum plate, electrodes, tap water, ground water and the like to be present in the electrolyte solution. In addition, secondary and tertiary ingredients may be added. Here, "second and tertiary ingredients" includes, for example, the ions of metals such 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.

[0201] The anodizing treatment conditions vary empirically according to the electrolyte solution used, although it is generally suitable for the 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/dm², 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.

[0202] 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.

[0203] Of these, as described in JP 54-12853 A and JP 48-45303 A, it is preferable to use a sulfuric acid solution as the electrolyte solution. The electrolyte 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 to 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 adding a compound such as aluminum sulfate to dilute sulfuric acid having a sulfuric acid concentration of 50 to 200 g/L.

[0204] Control of the electrolyte solution composition is typically carried out using a method similar to that employed in nitric acid electrolysis, as described above. That is, control is preferably achieved by preparing a matrix of the electrical conductivity, specific gravity and temperature or a matrix of the conductivity, ultrasonic wave propagation velocity and temperature with respect to a matrix of the sulfuric acid concentration and the aluminum ion concentration.

[0205] The electrolyte solution has a temperature of preferably 25 to 55° C., and more preferably 30 to 50° C.

[0206] 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.

[0207] When a direct current is applied to the aluminum plate, the current density is preferably 1 to 60 A/dm², and more preferably 5 to 40 A/dm².

[0208] 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/dm² at the start of anodizing treatment and to increase the current density to 30 to 50 A/dm² or more as anodizing treatment proceeds.

[0209] 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 alloca-

tion in this way will discourage the formation of burnt deposits, enabling high-speed anodization to be carried out.

[0210] 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.

[0211] By carrying out anodizing treatment under such conditions, a porous film having numerous micropores can be obtained. These micropores generally have an average diameter of about 5 to 50 nm and an average pore density of about 300 to 800 pores/ μm^2 .

[0212] The weight of the anodized layer is preferably 1 to 5 g/m². At a weight of 1 g/m² or more, scratches are not readily formed on the plate. A weight of not more than 5 g/m² does not require a large amount of electrical power, which is economically advantageous. An anodized layer weight of 1.5 to 4 g/m² 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/m².

[0213] The weight of the anodized layer on the opposite side to the surface having been subjected to the electrochemical graining treatment is preferably 0.1 to 1 g/m². At a weight of 0.1 g/m² 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/m² is economically advantageous.

[0214] Examples of electrolysis 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.

[0215] Of these, 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.

[0216] 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 on the upstream side of the aluminum plate 416 in the direction of advance by the plate 416 and an anodizing treatment tank 414 is disposed on the downstream side. 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 DC power supplies 434; and the aluminum plate 416 serves as the cathode. Hence, a cathodic reaction arises at the aluminum plate 416.

[0217] 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 poles of the DC power supplies 434; the aluminum plate 416 serves as the anode. Hence, an anodic reaction arises at the aluminum plate 416, and an anodized layer is formed on the surface of the aluminum plate 416.

[0218] The aluminum plate 416 is at a distance of preferably 50 to 200 mm from the cathode 430. The cathode 430 may be 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 by the aluminum plate 416 rather than to be a single electrode having a broad surface area.

[0219] 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 of the anodizing apparatus 410 through a discharge outlet 442.

[0220] To lower the voltage loss, an electrolyte solution 418 that collects in the power supplying cell 412 is set at a higher temperature and/or concentration than an electrolyte solution 426 that collects 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 on the anodized layer, the hardness of the anodized layer, the voltage, and the cost of the electrolyte solution.

[0221] 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.

[0222] 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 side of the aluminum plate 416 from 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 434 with their positive poles connected in common, thereby enabling control of the current distribution within the anodizing treatment tank 414.

[0223] 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

[0224] Sealing treatment may be carried out as required in the present invention to seal micropores in the anodized layer. Such treatment can enhance the developability (sensitivity) of the presensitized plate.

[0225] 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. 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.

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

[0226] The surface area can be measured using a simple BET-type surface area analyzer, such as Quantasorb (Yuasa Ionics Inc.).

[0227] 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 like that described in JP 9-244227 A, treatment with a sugar-containing aqueous solution like that described in JP 9-134002 A, treatment in a titanium and fluorine-containing aqueous solution like those described in JP 2000-81704 A and JP 2000-89466 A, and alkali metal silicate treatment like that described in U.S. Pat. No. 3,181,461.

[0228] 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. The aqueous solution of alkali metal silicate may include also a hydroxide compound such as sodium hydroxide, potassium hydroxide or lithium hydroxide in order to increase the pH.

[0229] 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.

[0230] The concentration of the alkali metal silicate solution is preferably 0.01 to 10 wt %, and more preferably 0.05 to 5.0 wt %.

[0231] 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 sensitivity (developability). 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 %.

[0232] It is desirable for the hexafluorozirconate solution to contain sodium dihydrogenphosphate in a concentration of preferably 0.01 to 3 wt %, and more preferably 0.1 to 0.3 wt %.

[0233] 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.

[0234] The sealing treatment temperature is preferably 20 to 90° C., and more preferably 50 to 80° C.

[0235] The sealing treatment time (period of immersion in the solution) is preferably 1 to 20 seconds, and more preferably 5 to 15 seconds.

[0236] 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, having an amino group, and a group selected from phosphinate group, phosphonate group and phosphate group mentioned in JP 11-231509 A.

[0237] Following sealing treatment, it is desirable to carry out the hydrophilizing treatment described below.

Hydrophilizing Treatment

[0238] 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 U.S. Pat. No. 2,946,638, the phosphomolybdate treatment described in U.S. Pat. No. 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 U.S. Pat. No. 3,307,951, the treatment involving the divalent metal salt of a lipophilic organic polymeric compound described in JP 58-16893 A and JP 58-18291 A, treatment like that described in U.S. Pat. No. 3,860,426 in which an aqueous metal salt (e.g., zinc acetate)-containing hydrophilic cellulose (e.g., carboxymethyl cellulose) undercoat is provided, and a treatment like that described in JP 59-101651 A in which a sulfo group-bearing water-soluble polymer is undercoated.

[0239] Additional examples of suitable hydrophilizing treatments include undercoating treatment using the phosphates mentioned in JP 62-19494 A, the water-soluble epoxy compounds mentioned in JP 62-33692 A, the phosphoric acid-modified starches mentioned in JP 62-97892 A, the diamine compounds mentioned in JP 63-56498 A, the inorganic or organic salts of amino acids mentioned in JP 63-130391 A, the carboxyl or hydroxyl group-bearing organic phosphonic acids mentioned in JP 63-145092 A, the amino group and phosphonic acid group-bearing com-

pounds mentioned in JP 63-165183 A, the specific carboxylic acid derivatives mentioned in JP 2-316290 A, the phosphate esters mentioned in JP 3-215095 A, the compounds having one amino group and one phosphorus oxo acid group mentioned in JP 3-261592 A, the aliphatic or aromatic phosphonic acids (e.g., phenylphosphonic acid) mentioned in JP 5-246171 A, the sulfur atom-bearing compounds (e.g., thiosalicylic acid) mentioned in JP 1-307745 A, and the phosphorus oxo acid group-bearing compounds mentioned in JP 4-282637 A.

[0240] Coloration with an acid dye as mentioned in JP 60-64352 A may also be carried out.

[0241] 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.

[0242] 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 U.S. Pat. No. 2,714,066 and U.S. Pat. No. 3,181,461.

[0243] Illustrative examples of suitable alkali metal silicates include sodium silicate, potassium silicate and lithium silicate. Suitable amounts of hydroxides such as sodium hydroxide, potassium hydroxide or lithium hydroxide may be included in the aqueous alkali metal silicate solution.

[0244] 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.

[0245] The amount of silicon adsorbed is preferably 1.0 to 10.0 mg/m². If the amount of silicon adsorbed falls within the above range, halftone dot non-image areas have excellent scumming resistance.

[0246] More specifically, shadow areas (halftone dot areas) in printed matter have a higher halftone dot area ratio (about 70 to 90%). In a lithographic printing plate, areas corresponding to halftone dot areas have a larger surface area for the image areas (image recording layer) but a relatively smaller surface area for the non-image areas (exposed areas of the support). In such a case, a phenomenon easily occurs during printing in which ink on an image area comes in contact with ink on an adjacent image area (that is, the former is mixed with the latter), part of the ink adheres to the non-image area located therebetween, and the non-image area in a printed material is filled with ink (namely stained with ink).

[0247] However, by carrying out hydrophilizing treatment so that the amount of silicon adsorbed onto the surface of a

lithographic printing plate support falls within the above range, non-image areas have improved hydrophilicity. Therefore, when the thus obtained lithographic printing plate support is used to manufacture a lithographic printing plate and printing is carried out with the lithographic printing plate, halftone dot non-image areas can have enhanced scumming resistance.

[0248] For example, an aqueous solution having a sodium silicate concentration of 1 to 5 wt % is used to carry out hydrophilizing treatment so that the amount of silicon can fall within the above range. It is particularly preferable to use disodium disilicate as the sodium silicate.

[0249] 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.

[0250] 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 —NH₂ groups, —COOH groups and sulfo groups.

Drying

[0251] 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.

[0252] 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.

[0253] The drying time is preferably at least 1 second, and preferably at least 2 seconds, but preferably not more than 20 seconds, and more preferably not more than 15 seconds.

Presensitized Plate

[0254] The lithographic printing plate support obtained by the present invention can be formed into a presensitized plate of the present invention by providing the image recording layer thereon. A photosensitive composition is used in the image recording layer.

[0255] 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

[0256] 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 that from an infrared laser into heat, which efficiently eliminates interactions that lower the alkali solubility of the alkali-soluble polymeric compound.

[0257] 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 hydroxyl group, a sulfonamide group ($-\text{SO}_2\text{NH}-\text{R}$, wherein R is a hydrocarbon group) or an active imino group ($-\text{SO}_2\text{NHCOR}$, $-\text{SO}_2\text{NHSO}_2\text{R}$ or $-\text{CONHSO}_2\text{R}$, wherein R is as defined above), are especially preferred on account of their solubility in alkaline developers.

[0258] For an excellent film formability with exposure to light from an infrared laser, resins having phenolic hydroxyl groups are 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.

[0259] Additional preferred examples include the polymeric compounds mentioned in JP 2001-305722 A (especially paragraphs [0023] to [0042]), the polymeric compounds having recurring units of general formula (I) mentioned in JP 2001-215693 A, and the polymeric compounds mentioned in JP 2002-311570 A (especially paragraph [0107]).

[0260] To provide a good recording sensitivity, the photothermal conversion substance is preferably a pigment or dye that absorbs light in the infrared range at a wavelength of 700 to 1200 nm. Illustrative examples of suitable dyes include azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, pyrylium salt and metal-thiolate complexes (e.g., nickel-thiolate complexes). Of these, cyanine dyes are preferred. The cyanine dyes of general formula (I) mentioned in JP 2001-305722 A are especially preferred.

[0261] A dissolution inhibitor may be included in thermal positive-type photosensitive compositions. Preferred examples of dissolution inhibitors include those mentioned in paragraphs [0053] to [0055] of JP 2001-305722 A.

[0262] 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 those mentioned in paragraphs [0056] to [0060] of JP 2001-305722 A are preferred.

[0263] Use of the photosensitive compositions described in detail in JP 2001-305722 A is desirable for additional reasons as well.

[0264] The thermal positive-type image recording layer is not limited to a single layer, and may have a two-layer construction.

[0265] Preferred examples of image recording layers with a two-layer construction (also referred to as "multilayer-type image recording layers") include those of a type provided on the side close to the support with a bottom layer ("layer A") of excellent press life and solvent resistance, and provided on layer A with a layer ("layer B") having an excellent positive image-forming ability. 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.

[0266] Preferred examples of resins that may be used in layer A include polymers that contain as a copolymerizable ingredient a monomer having a sulfonamide group, an active imino group or a phenolic hydroxyl group; such polymers have an excellent press life and solvent resistance. Preferred examples of resins that may be used in layer B include phenolic hydroxyl group-bearing resins which are soluble in aqueous alkali solutions.

[0267] 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 mentioned in paragraphs [0062] to [0085] of JP 2002-3233769 A. The additives mentioned in paragraphs [0053] to [0060] in JP 2001-305722 A are also suitable for use.

[0268] The components and proportions thereof in each of layers A and B may be selected as described in JP 11-218914 A.

Intermediate Layer

[0269] 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 mentioned in paragraph [0068] of JP 2001-305122 A.

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

Thermal Negative-Type Photosensitive Compositions

[0270] 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

[0271] 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-like polymerization and curing of the radical polymerizable compound.

[0272] 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 mentioned in paragraphs [0017] to [0019] of JP 2001-133969 A.

[0273] Preferred radical generators include onium salts. The onium salts mentioned in paragraphs [0030] to [0033] of JP 2001-133969 A are especially preferred.

[0274] Exemplary radical polymerizable compounds include compounds having one, and preferably two or more, terminal ethylenically unsaturated bonds.

[0275] 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 *c*-arboxyl groups in side chains are especially preferred because they provide an excellent balance of film strength, sensitivity and developability.

[0276] Radical polymerizable compounds and binder polymers that may be used include those mentioned specifically in paragraphs [0036] to [0060] of JP 2001-133969 A.

[0277] Thermal negative-type photosensitive compositions preferably contain additives mentioned in paragraphs [0061] to [0068] of JP 2001-133969 A (e.g., surfactants for enhancing coatability).

[0278] The methods described in detail in JP 2001-133969 A can be used to form a polymerizable layer and to manufacture a lithographic printing plate having such a layer.

Acid-Crosslinkable Layer

[0279] 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 a thermal acid generator, thereby generating an acid which causes the crosslinker and the alkali-soluble polymeric compound to react and cure.

[0280] The photothermal conversion substance is exemplified by the same substances as can be used in the polymerizable layer.

[0281] Exemplary thermal acid generators include photopolymerization photoinitiators, dye photochromogenic substances, and heat-degradable compounds such as acid generators which are used in microresists and the like.

[0282] Exemplary crosslinkers include hydroxymethyl or alkoxymethyl-substituted aromatic compounds, compounds having N-hydroxymethyl, N-alkoxymethyl or N-acyloxymethyl groups, and epoxy compounds.

[0283] Exemplary alkali-soluble polymeric compounds include novolak resins and polymers having hydroxyaryl groups in side chains.

Photopolymer-Type Photosensitive Compositions

[0284] Photopolymer-type photosensitive compositions contain an addition polymerizable compound, a photopolymerization initiator and a polymer binder.

[0285] Preferred addition polymerizable compounds include compounds having an addition-polymerizable ethylenically unsaturated bond. Ethylenically unsaturated bond-containing compounds are compounds which have a terminal ethylenically unsaturated bond. These include compounds having the chemical form of monomers, prepolymers, and mixtures 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.

[0286] Preferred addition polymerizable compounds include also urethane-type addition-polymerizable compounds.

[0287] 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 initiation systems mentioned in paragraphs [0021] to [0023] of JP 2001-22079 A.

[0288] The polymer binder, inasmuch as it must function as a film-forming agent for the photopolymerizable photosensitive composition and must also allow the image recording layer to dissolve in an alkaline developer, may be an organic polymer which is soluble or swellable in an aqueous alkali solution. Preferred examples of such organic polymers include those mentioned in paragraphs [0036] to [0063] of JP 2001-22079 A.

[0289] It is preferable for the photopolymer-type photopolymerizable photosensitive composition to include the additives mentioned in paragraphs [0079] to [0088] of JP

2001-22079 A (e.g., surfactants for improving coatability, colorants, plasticizers, thermal polymerization inhibitors).

[0290] 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.

[0291] 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

[0292] Conventional negative-type photosensitive compositions contain a diazo resin or a photo-crosslinkable resin. Of these, photosensitive compositions which contain a diazo resin and an alkali-soluble or swellable polymeric compound (binder) are preferred.

[0293] The diazo resin is exemplified by the 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 in which the content of hexamer and larger oligomers mentioned in JP 59-78340 A is at least 20 mol % are especially preferred.

[0294] Exemplary binders include copolymers containing acrylic acid, methacrylic acid, crotonic acid or maleic acid as an essential ingredient. Specific examples include the multi-component copolymers of monomers such as 2-hydroxyethyl(meth)acrylate, (meth)acrylonitrile and (meth)acrylic acid mentioned in JP 50-118802 A, and the multi-component copolymers of alkyl acrylates, (meth)acrylonitrile and unsaturated carboxylic acids mentioned in JP 56-4144 A.

[0295] 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, the compounds such as development promoters, and the surfactants for enhancing coatability mentioned in paragraphs [0014] to [0015] of JP 7-281425 A.

[0296] 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

[0297] 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.

[0298] Illustrative examples of the o-quinonediazide compound include esters of 1,2-naphthoquinone-2-diazo-5-sulfonylchloride and a phenol-formaldehyde resin or a cresol-formaldehyde resin, and the esters of 1,2-naphtho-

quinone-2-diazo-5-sulfonylchloride and pyrogallol-acetone resins mentioned in U.S. Pat. No. 3,635,709.

[0299] 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 carboxyl group-bearing polymers mentioned in JP 7-36184 A, the phenolic hydroxyl group-bearing acrylic resins mentioned in JP 51-34711 A, the sulfonamide group-bearing acrylic resins mentioned in JP 2-866 A, and urethane resins.

[0300] Conventional positive-type photosensitive compositions preferably contain as additives the compounds such as sensitivity regulators, print-out agents and dyes mentioned in paragraphs [0024] to [0027] of JP 7-92660 A, and surfactants for enhancing coatability such as those mentioned in paragraph [0031] of JP 7-92660 A.

[0301] 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 above-described conventional negative-type photosensitive layer.

Non-Treatment Type Photosensitive Compositions

[0302] 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.

[0303] 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.

[0304] 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 thermoplastic finely divided 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. 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.

[0305] The finely divided polymer preferably has reactive functional groups.

[0306] 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.

[0307] Illustrative examples of sulfonic acid-generating polymers that may be used in sulfonic acid generating polymer-containing photosensitive compositions include the polymers having in side chains, sulfonate ester groups, disulfone groups or sec- or tert-sulfonamide groups described in JP 10-282672 A.

[0308] 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 hydroxyl, carboxyl, hydroxyethyl, hydroxypropyl, amino, aminoethyl, aminopropyl or carboxymethyl groups; and hydrophilic sol-gel conversion-type binder resins.

[0309] 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 can be used as the method of forming a non-treatment type image recording layer and the associated platemaking and printing methods.

Back Coat

[0310] If necessary, the presensitized plate of the invention obtained by providing any of the various image recording layers on a lithographic printing plate support obtained according to the invention may be provided on the back 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

[0311] The presensitized plate prepared using a lithographic printing plate support obtainable according to this invention is then subjected to any of various treatment methods depending on the type of image recording layer, thereby obtaining a lithographic printing plate.

[0312] 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 helium-neon lasers (He—Ne lasers), argon lasers, krypton lasers, helium-cadmium lasers, KrF excimer lasers, semiconductor lasers, YAG lasers and YAG-SHG lasers.

[0313] Following exposure as described above, when 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 liquid developer in order to obtain the lithographic printing plate.

[0314] The liquid developer is preferably an alkaline developer, and more preferably an alkaline aqueous solution which is substantially free of organic solvent.

[0315] Liquid developers which are substantially free of alkali metal silicates are also preferred. One example of a suitable method of development using a liquid developer

that is substantially free of alkali metal silicates is the method described in detail in JP 11-109637 A.

[0316] Liquid developers which contain an alkali metal silicate can also be used.

EXAMPLES

[0317] Hereinafter, the present invention is described in detail by way of examples. However, the present invention is not limited thereto.

1. Manufacture of Aluminum Plate Embossing Roll

[0318] 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 A.

[0319] A roll for metal rolling RP53 (hardness of Hv97) manufactured by Kanto Special Steel Works, Ltd. was successively subjected to the treatments (1) to (5) below, yielding an aluminum plate embossing roll B.

(1) Mirror-Like Finishing

[0320] Buffing was carried out as the mirror-like finishing process, thereby removing marks left by the grindstone used to polish the surface of the roll. On the polished surface, the average roughness R_a was $0.2\ \mu\text{m}$ and the maximum height R_{max} was $1\ \mu\text{m}$. The average roughness R_a and the maximum height R_{max} were measured according to the measurement of the arithmetic average surface roughness R_a and maximum height R_y defined in JIS B0601-1994.

(2) Blasting

[0321] 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 $2\ \text{kgf/cm}^2$ ($1.96 \times 10^5\ \text{Pa}$) and the average surface roughness R_a of the surface after the air blasting was $0.8\ \mu\text{m}$.

(3) Degreasing

[0322] The roll was immersed for 30 seconds in a degreasing tank containing a 30°C . degreasing solution, and surface oil was removed from the roll with the solution. The roll was then rinsed with water, after which air was blown over it to remove moisture.

(4) Electrolytic Treatment

[0323] The roll was subjected to electrolytic treatment 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 by the continuous application of a direct current at a current density of $30\ \text{A/dm}^2$ using the roll as the anode. The amount of electricity used in electrolytic treatment was $10,000\ \text{C/dm}^2$.

[0324] The current waveform was three-phase full-wave rectified, then passed through a filter circuit and used as direct current having a ripple component of 5% or less. Lead was used as the counter electrode. The roll was placed upright in the electrolyte solution, and a cylindrical lead electrode was arranged 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

[0325] Next, chromium plating treatment was carried out 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 by the continuous application of a direct current at a current density of 40 A/dm² using the roll as the cathode. The plating treatment time was set such as to give a plating thickness of 6 μm.

[0326] The current waveform was three-phase full-wave rectified, then passed through a filter circuit and used as direct current having a ripple component of 5% or less. Lead was used as the counter electrode. The roll was placed upright in the electrolyte solution, and a cylindrical lead electrode was arranged 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

[0327] A melt was prepared from an aluminum alloy comprising the respective components (wt %) shown in Table 1, with the balance being aluminum and inadvertent 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 on average 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, thereby obtaining aluminum plates 1-3 each having a thickness of 0.3 mm and a width of 1,060 mm. Cold rolling was carried out without heat treatment at 500° C. in the continuous annealing furnace, thereby obtaining an aluminum plate 7 having a thickness of 0.3 mm and a width of 1,060 mm.

[0328] Aluminum plates 4-6 were respectively obtained by repeating the method used for the aluminum plates 1-3 except that the aluminum plate embossing roll A obtained above was used in the cold rolling.

[0329] An aluminum plate 8 was obtained by repeating the method used for the aluminum plate 7 except that the aluminum plate embossing roll B obtained 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
7	0.080	0.300	0.000	0.001	0.000	0.001	0.003	0.021

3. Fabrication of Lithographic Printing Plate Support

Examples 1-1 to 1-35, 3-1 to 3-5 and Comparative Example 1

[0330] The aluminum plates obtained in the above processes were subjected to surface treatments described below to obtain lithographic printing plate supports shown in Tables 2-1 to 2-5.

Surface Treatment

[0331] The aluminum plates were successively subjected to the surface treatments (a) to (j) in Examples 1-1 to 1-35 and Comparative Example 1, and the surface treatments (a) to (i) and (k) in Examples 3-1 to 3-5.

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

[0332] Etching was carried out by spraying each aluminum plate 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/m².

[0333] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

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

[0334] Desmutting was carried out by spraying each aluminum plate 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. for 5 seconds from a spray line. Wastewater from the subsequently described anodizing treatment step (i) was used here as the aqueous sulfuric acid solution.

[0335] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

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

[0336] Electrochemical graining treatment was carried out on the aluminum plates subjected to the treatment (b) by utilizing aqueous solutions having hydrochloric acid concentrations, nitric acid concentrations and aluminum ion concentrations shown in Tables 2-1 and 2-2 (temperature: 35° C.) for the first electrolyte, controlling the current through inverter control using an IGBT device, and utilizing a power supply that can generate an alternating current of any waveform. The hydrochloric acid concentration and aluminum ion concentration of the first electrolyte were adjusted with hydrochloric acid and aluminum chloride. The nitric acid concentration was adjusted with nitric acid.

[0337] The waveform of the alternating current applied to each aluminum plate, current rise time when the alternating current applied to each aluminum plate had a trapezoidal waveform, frequency of the alternating current applied to each aluminum plate, amount of electricity, current ratio and duty ratio were as shown in Tables 2-1 and 2-2. The amount of electricity refers to the total amount of electricity used during the anodic reaction on the aluminum plate. The current ratio QR/QF refers to the ratio between the total amount of electricity QR used during the cathodic reaction on the aluminum plate and the total amount of electricity QF used during the anodic reaction on the aluminum plate in the main electrolytic cell.

[0338] The current density during the anodic reaction on each aluminum plate at the alternating current peaks was 25 A/dm².

[0339] The concentration control of the electrolyte solution was carried out by adding hydrochloric acid in an amount corresponding to the amount of applied electricity and replenishment water including a desired concentration of nitric acid added thereto in advance, according to a predetermined data table. For the concentration control of the electrolyte solution, the relation between the electrical conductivity of the electrolyte solution and the ultrasonic wave propagation velocity was established in accordance with the composition of the electrolyte solution to prepare the data table and the amounts of hydrochloric acid and replenishment water to be added were adjusted by feedback control based on the measurement results on the electrical conductivity of the electrolyte solution and the ultrasonic wave propagation velocity in the electrolyte solution.

[0340] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

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

[0341] Etching was carried out by spraying each aluminum plate 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 as shown in Tables 2-3 to 2-5.

[0342] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

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

[0343] Desmutting was carried out by spraying each aluminum plate 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. for 5 seconds from a spray line. Wastewater from the subsequently described anodizing treatment step (i) was used here as the aqueous sulfuric acid solution.

[0344] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

(f) Electrochemical Graining Treatment Using Alternating Current in Aqueous Acidic Solution (Second Electrochemical Graining)

[0345] Electrochemical graining treatment was carried out on the aluminum plates subjected to the treatments (a)-(e) by utilizing aqueous solutions having hydrochloric acid concentrations, nitric acid concentrations and aluminum ion concentrations shown in Tables 2-3 to 2-5 (temperature: 35°

C.) for the second electrolyte, controlling the current through inverter control using an IGBT device, and utilizing a power supply that can generate an alternating current of any waveform. The hydrochloric acid concentration and the aluminum ion concentration of the second electrolyte were adjusted with hydrochloric acid and aluminum chloride. When the second electrolyte contains nitric acid, the nitric acid concentration was adjusted with nitric acid.

[0346] The waveform of the alternating current applied to each aluminum plate, current rise time when the alternating current applied to each aluminum plate had a trapezoidal waveform, frequency of the alternating current applied to each aluminum plate, amount of electricity, current ratio and duty ratio were as shown in Tables 2-3 to 2-5.

[0347] In the second electrochemical graining treatment, the current density during the anodic reaction on each aluminum plate at the alternating current peaks was 50 A/dm².

[0348] For the concentration control of the electrolyte solution, was used a method in which hydrochloric acid and water were added in amounts proportional to the amounts of applied electricity according to the predetermined data table, multi-component concentrations were measured using the predetermined data table that defines the relation between the solution composition (hydrochloric acid concentration and aluminum ion concentration), ultrasonic wave propagation velocity in the solution and the electrical conductivity in the solution, and the amounts of hydrochloric acid and water to be added were corrected based on the obtained results. When the second electrolyte contained nitric acid, its concentration was also controlled while adding nitric acid in the same manner as hydrochloric acid.

[0349] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

(g) Etching in Aqueous Alkali Solution (Third Etching)

[0350] Etching was carried out by spraying each aluminum plate 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 material removed by etching from the surface of each aluminum plate subjected to electrochemical graining treatment was as shown in Tables 2-3 to 2-5.

[0351] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

(h) Desmutting in Aqueous Acidic Solution (Third Desmutting)

[0352] Desmutting was carried out by spraying each aluminum plate 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. for 5 seconds from a spray line. Wastewater from the subsequently described anodizing treatment step (i) was used here as the aqueous sulfuric acid solution.

[0353] The solution was then removed from each plate with nip rollers. After removal of the solution, the plate was not rinsed with water but was subjected to anodizing treatment (i).

(i) Anodizing Treatment

[0354] 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 on each aluminum plate during the anodic reaction was 15 A/dm². The final weight of the anodized layer was 2.7 g/m².

[0355] The solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers.

(j) Hydrophilizing Treatment 1

[0356] Hydrophilizing treatment was carried out by immersing each aluminum plate for 10 seconds in 1 wt % aqueous solution of disodium trisilicate (solution temperature, 20° C.). The amount of silicon on the surface of each aluminum plate, as measured by a fluorescent x-ray analyzer, was 3.5 mg/m².

[0357] Next, the solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers. Further, each plate was dried by blowing 90° C. air across it for 10 seconds, thereby obtaining a lithographic printing plate support.

(k) Hydrophilizing Treatment 2

[0358] Hydrophilizing treatment was carried out by immersing each aluminum plate for 8 seconds in 4.0 wt % aqueous solution of disodium disilicate (solution temperature, 22° C.). The amount of silicon on the surface of each aluminum plate, as measured by a fluorescent x-ray analyzer, was 5.3 mg/m².

[0359] Next, the solution was removed from each plate with nip rollers. Rinsing treatment was then carried out for 5 seconds using fan-like sprays of water directed at the plate from spray tips mounted on spray lines, and the rinse water was removed from the plate with nip rollers. Further, each plate was dried by blowing 90° C. air across it for 10 seconds, thereby obtaining a lithographic printing plate support.

Examples 2-1 to 2-3

[0360] Lithographic printing plate supports in Examples 2-1 to 2-3 were obtained by the same method as in Examples 1-29 to 1-31 except that the treatment (z) to be described below was carried out prior to the treatment (a) and the amount of material removed by etching from the surface of each aluminum plate to be subsequently subjected to electrochemical graining treatment in (a) was changed to 10 g/m².

(z) Mechanical Graining Treatment

[0361] The device as shown in FIG. 6 was used to carry out mechanical graining treatment by rotating nylon roller brushes while a suspension containing an abrasive (pumice) and water (specific gravity: 1.12) was supplied to the surface of each aluminum plate as an abrasive slurry. In FIG. 6, reference numeral 1 is an aluminum plate, 2 and 4 are roller brushes, 3 is an abrasive slurry, and 5, 6, 7 and 8 are support rollers. The average particle size of the abrasive was 30 μm. The nylon brush was made of nylon 6.10 and had a bristle length of 50 mm and a bristle diameter of 0.3 mm. For the nylon brush, the bristles were densely implanted in holes formed in a stainless steel cylinder having a diameter of 300 mm. Three rotating brushes were used. The distance between the two support rollers (diameter: 200 mm) under the brushes was 300 mm. The brushes were rotated in the same direction as the direction in which the aluminum plate was moved. The brushes were rotated at 200 rpm.

[0362] The surface roughness R_a after the mechanical graining treatment was 0.45 μm.

4. Surface Examination of Lithographic Printing Plate Supports

[0363] The surface profile of each of the lithographic printing plate supports obtained in Examples 1-1 to 1-35, 2-1 to 2-3 and 3-1 to 3-5 were examined under a scanning electron microscope (JSM-5500, manufactured by JEOL, Ltd.; the same applies below) at a magnification of 50,000×, and fine asperities each having an average aperture diameter of 0.05 to 0.3 μm were found to have been uniformly and densely formed on the surface thereof.

[0364] The surface profile of each of the above lithographic printing plate supports was also examined under the scanning electron microscope at a magnification of 2,000×, and asperities each having an average aperture diameter of 1 to 5 μm were found to have been uniformly formed on the surface thereof.

[0365] The fine asperities each having an average aperture diameter of 0.05 to 0.3 μm were superimposed on the asperities each having an average aperture diameter of 1 to 5 μm.

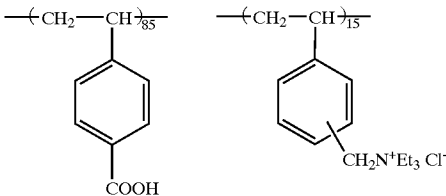
[0366] On the other hand, the surface profile of the lithographic printing plate support obtained in Comparative Example 1 was examined in the same manner as above at a magnification of 50,000×, and asperities were found to have been formed on the surface, but they had each a smaller depth and a less uniform average aperture diameter than in Examples.

[0367] The surface profile of this lithographic printing plate support was also examined under the scanning electron microscope at a magnification of 2,000×, and larger asperities than those observed at the magnification of 50,000× were found to have been formed on the surface in a nonuniform manner.

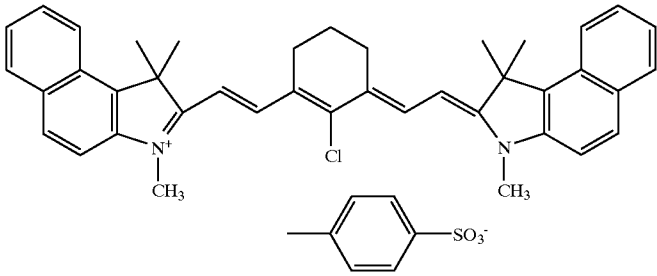
5. Fabrication of Presensitized Plate

[0368] Presensitized 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 in Examples 1-1 to 1-35, 2-1 to 2-3 and Comparative Example 1. Before providing the image recording layer, an undercoat was formed on each support as follows.

[0369] An undercoating solution A of the composition indicated below was applied onto each 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/m².

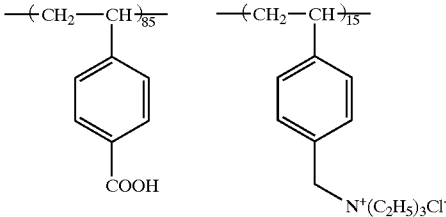
Composition of Undercoating Solution A	
Polymeric compound of the following formula	0.3 g
	
MOLECULAR WEIGHT, 28,000	
Methanol	100 g
Water	1 g

[0370] In addition, a heat-sensitive layer-forming coating solution A1 of the following composition was prepared. The heat-sensitive layer-forming coating solution A1 was applied onto each undercoated lithographic printing plate support to a coating weight after drying (heat-sensitive layer coating weight) of 1.8 g/m² and dried so as to form a heat-sensitive layer (thermal positive-type image recording layer), thereby giving each presensitized plate.

Composition of Heat Sensitive Layer-Forming Coating Solution A1	
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 changed to 6-hydroxy-β-naphthalenesulfonic acid	0.02 g
Fluorocarbon surfactant (Megafac F-780F, available from Dainippon Ink and Chemicals, Inc.; 30 wt % solids)	0.0045 g (solids)
Fluorocarbon surfactant (Megafac F-781F, available from Dainippon Ink and Chemicals, Inc.; 100 wt % solids)	0.035 g
Methyl ethyl ketone	12 g

[0371] Presensitized 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 in Examples 3-1 to 3-5. Before providing the image recording layer, an undercoat was formed on each support as follows.

[0372] An undercoating solution B of the composition indicated below was applied onto each 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/m².

Composition of Undercoating Solution B	
Polymeric compound of the following formula	0.3 g
	
MOLECULAR WEIGHT, 26,000	

-continued

Composition of Undercoating Solution B	
Methanol	100 g
Water	1 g

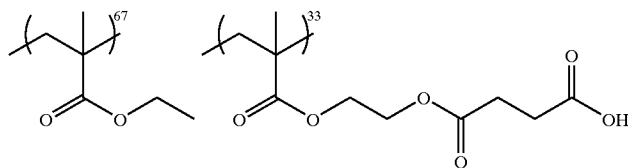
[0373] In addition, an image recording layer-forming coating solution B1 of the composition indicated below was applied onto each undercoated lithographic printing plate support with a wire bar so that the coating weight after drying of 0.85 g/m² was obtained and dried at 140° C. for 50 seconds.

[0374] Thereafter, another image recording layer-forming coating solution B2 of the composition indicated below was applied onto each lithographic printing plate support with a wire bar so that the coating weight after drying of 0.25 g/m² was obtained and dried at 140° C. for 1 minute. A multi-layered thermal positive-type image recording layer was thus formed on each support to obtain each presensitized plate.

Composition of Image Recording Layer-Forming Coating Solution B1	
N-(4-aminosulfonylphenyl)methacrylamide/acrylonitrile/methyl methacrylate copolymer (molar ratio, 36/34/30, weight-average molecular weight, 50,000)	1.920 g
Novolak made from m-cresol and p-cresol (m-cresol/p-cresol = 6/4; weight-average molecular weight, 4,000)	0.213 g
Cyanine dye A of the above formula	0.032 g
p-Toluenesulfonic acid	0.008 g
Tetrahydrophthalic anhydride	0.19 g
Bis-p-hydroxyphenylsulfone	0.126 g
2-Methoxy-4-(N-phenylamino)benzenediazonium hexafluorophosphate	0.032 g
Victoria Pure Blue BOH in which counteranion was changed to 1-naphthalenesulfonic acid anion	0.078 g
Fluorocarbon surfactant (Megafac F-780, available from Dainippon Ink and Chemicals, Inc.)	0.020 g
γ -Butyrolactone	13.18 g
Methyl ethyl ketone	25.41 g
1-Methoxy-2-propanol	12.97 g

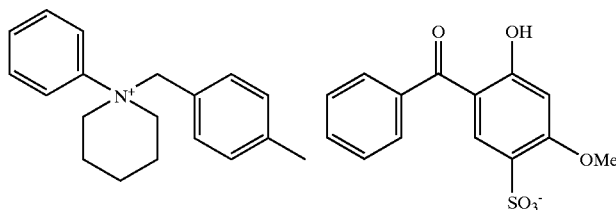
[0375]

Composition of Image Recording Layer-Forming Coating Solution B2	
Novolak made from phenol, m-cresol and p-cresol (phenyl/m-cresol/p-cresol = 5/3/2; weight-average molecular weight, 4,000)	0.274 g
Cyanine dye A of the above formula	0.029 g
Solution in methyl ethyl ketone of 30 wt % structural polymer C of the following formula	0.14 g



MOLECULAR WEIGHT 50,000
STRUCTURAL POLYMER C

Quarternary ammonium salt D of the following formula	0.004 g
--	---------

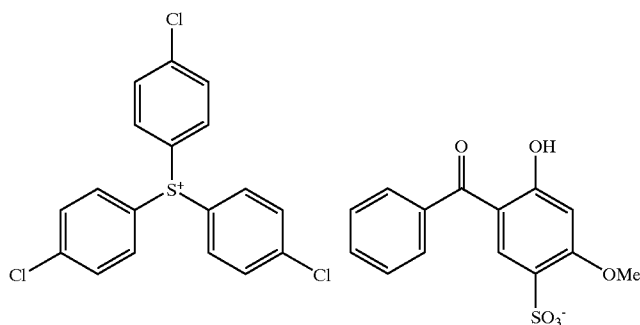


QUARTERNARY AMMONIUM SALT D

Sulfonium salt E of the following formula	0.065 g
---	---------

-continued

Composition of Image Recording Layer-Forming Coating Solution B2



SULFONIUM SALT E

Fluorocarbon surfactant (Megafac F-780, available from Dainippon Ink and Chemicals, Inc.)	0.004 g
Fluorocarbon surfactant (Megafac F-782, available from Dainippon Ink and Chemicals, Inc.)	0.020 g
Methyl ethyl ketone	10.39 g
1-Methoxy-2-propanol	20.98 g

6. Evaluation of Presensitized Plate

[0376] The press life, cleaner press life (chemical resistance), scumming resistance and shininess of the lithographic printing plates and scumming resistance of halftone dot non-image areas were evaluated according to the following methods.

(1) Press Life

[0377] Trendsetter manufactured by Creo was used to form an image on each presensitized plate at a drum rotation speed of 150 rpm and a beam intensity of 10 W.

[0378] Thereafter, PS Processor 940H manufactured by Fuji Photo Film Co., Ltd. which contained an alkaline developer of the composition described below was used to develop each presensitized plate for 20 seconds while maintaining the developer at 30° C., whereby each lithographic printing plate was obtained. The sensitivity of each presensitized plate was excellent.

Composition of Alkaline Developer

D-sorbit	2.5 wt %
Sodium hydroxide	0.85 wt %
Polyethyleneglycol lauryl ether (weight-average molecular weight 1000)	0.5 wt %
Water	96.15 wt %

[0379] Each of the obtained lithographic printing plates was set on Lithrone Press (manufactured by Komori Corporation) for printing using black ink DIC-GEOS (N) available from Dainippon Ink and Chemicals, Inc. Press life was evaluated by the number of sheets that were printed until the density of solid images began to decline on visual inspection.

[0380] Results are shown in Tables 2-3 to 2-5. In Tables 2-3 to 2-5, the following criteria were used for evaluation.

[0381] A: The number of printed sheets is 30,000 or above;

[0382] A-B: The number of printed sheets is 20,000 or above but less than 30,000;

[0383] B: The number of printed sheets is 10,000 or above but less than 20,000;

[0384] C: The number of printed sheets is less than 10,000.

(2) Cleaner Press Life (Chemical Resistance)

[0385] The cleaner press life was evaluated as in (1) Press life except that, each time 5000 sheets were printed, a multi-purpose cleaner available from Fuji Photo Film Co., Ltd. was applied onto the surface of the image recording layer and wiped it off with water one minute later. The cleaner press life was evaluated based on the number of sheets that were printed until the ink concentration (reflection density) was decreased by 0.1 from the time when printing had been started. The cleaner press life was used as a method for evaluating the press life.

[0386] Results are shown in Tables 2-3 to 2-5. In Tables 2-3 to 2-5, the following criteria were used for evaluation.

[0387] A: The number of printed sheets is 10,000 or above;

[0388] A-B: The number of printed sheets is 6,000 or above but less than 10,000;

[0389] B: The number of printed sheets is 3,000 or above but less than 6,000.

(3) Scumming Resistance

[0390] Each lithographic printing plate as used in the evaluation of (1) Press life was set on Mitsubishi DAIYA F2 Press (manufactured by Mitsubishi Heavy Industries, Ltd.) for printing using red ink DIC-GEOS (s). After printing 10,000 sheets, stains on the blanket were evaluated visually.

[0391] Results are shown in Tables 2-3 to 2-5. In Tables 2-3 to 2-5, the following criteria were used for evaluation.

[0392] A: very few stains on the blanket;

[0393] A-B: a few stains on the blanket;

[0394] C: the blanket is stained and printed matter is apparently stained.

(4) Shininess

[0395] Each lithographic printing plate as used in the evaluation of (1) Press Life was set on Lithrone Press (manufactured by Komori Corporation) and the shininess in the non-image areas of each plate surface was observed visually while reducing the amount of fountain solution to be added. The shininess was evaluated in terms of the amount of fountain solution supplied when each plate began to shine (as to whether the amount of water was readily checked).

[0396] Results are shown in Tables 2-3 to 2-5. In Tables 2-3 to 2-5, the following criteria were used for evaluation.

[0397] A: When the amount of fountain solution to be added is reduced, the plate surface does not readily shine;

[0398] B: When the amount of fountain solution to be added is reduced, the plate surface readily shines and it is a little difficult to visually adjust the amount of fountain solution.

(5) Scumming Resistance of Halftone Dot Image Areas

[0399] Each of the lithographic printing plates obtained above was mounted on a printing press SOR-M manufactured by Heidelberg. An aqueous solution containing 3 wt %

of IF102 (manufactured by Fuji Photo Film Co., Ltd.) for the fountain solution and values (N) black ink available from Dainippon Ink and Chemicals, Inc. were used to carry out printing. The amount of fountain solution was gradually decreased from a reference water amount and to what degree scumming occurred in shadow areas (halftone dot area ratio: 80%) due to the contact of ink in adjacent image areas was visually evaluated.

[0400] As is clear from Tables 2-3 to 2-5, every lithographic printing plate using a lithographic printing plate support obtained by the method of manufacturing a lithographic printing plate support according to the present invention (Examples 1-1 to 1-35, 2-1 to 2-3 and 3-1 to 3-5) had excellent scumming resistance and a long press life. The cleaner press life and shininess were also excellent.

[0401] On the other hand, when using the lithographic printing plate support obtained in Comparative Example 1 in which the total amount of electricity when the aluminum plate served as the anode in the electrochemical graining treatment was too large, the lithographic printing plate obtained by using the above support was inferior in scumming resistance.

[0402] Each of the lithographic printing plates using the lithographic printing plate supports obtained in Examples 3-1 to 3-5 was more excellent in the scumming resistance of the halftone dot non-image areas than each of the lithographic printing plates using the lithographic printing plate supports obtained in Examples 1-1 to 1-35 and 2-1 to 2-3. In other words, these plates were excellent in all of the press life, scumming resistance, cleaner press life, shininess and scumming resistance of halftone dot non-image areas.

TABLE 2-1

	Aluminum plate	Mechanical graining	First etching Amount	First electrochemical graining								Frequency (Hz)
			of aluminum dissolved (g/m ²)	Hydrochloric acid concentration (g/L)	Nitric acid concentration (g/L)	Aluminum ion concentration (g/L)	Waveform	Current rise time (msec)	Amount of electricity (C/dm ²)	Duty ratio	Current ratio	
EX1-1	5	Unperformed	3	7.5	1	5	Sinusoidal	—	200	0.5	0.95	60
EX1-2	5	Unperformed	3	7.5	3	5	Sinusoidal	—	200	0.5	0.95	60
EX1-3	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-4	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-5	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-6	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-7	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-8	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	1.00	60
EX1-9	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	1.00	60
EX1-10	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	1.00	50
EX1-11	5	Unperformed	3	7.5	5	5	Sinusoidal	—	150	0.5	0.95	60
EX1-12	5	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-13	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-14	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-15	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-16	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-17	5	Unperformed	3	7.5	8	5	Sinusoidal	—	200	0.5	0.95	60
EX1-18	4	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-19	6	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-20	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-21	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-22	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60

[0403]

TABLE 2-2

Aluminum plate	Mechanical graining	First etching Amount	First electrochemical graining					Current rise time (msec)	Amount of electricity (C/dm ²)	Duty ratio	Current ratio	Frequency (Hz)
			of aluminum dissolved (g/m ²)	Hydrochloric acid concentration (g/L)	Nitric acid concentration (g/L)	Aluminum ion concentration (g/L)	Waveform					
EX1-23	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-24	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-25	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX1-26	5	Unperformed	3	7.5	5	5	Sinusoidal	—	200	0.5	0.95	50
EX1-27	5	Unperformed	3	7.5	5	5	Trapezoidal	0.8	200	0.5	0.95	60
EX1-28	1	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-29	2	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-30	2	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-31	2	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-32	3	Unperformed	3	7.5	5	5	Sinusoidal	—	250	0.5	0.95	60
EX1-33	1	Unperformed	3	10.0	5	8	Triangular	14.0	270	0.5	0.95	30
EX1-34	2	Unperformed	3	10.0	5	8	Triangular	16.0	270	0.5	0.95	30
EX1-35	1	Unperformed	3	10.0	5	8	Triangular	15.0	270	0.5	0.95	30
EX2-1	2	Performed	10	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX2-2	2	Performed	10	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
EX2-3	2	Performed	10	7.5	5	5	Sinusoidal	—	200	0.5	0.95	60
CE1	1	Unperformed	3	7.5	5	5	Sinusoidal	—	900	0.5	0.95	60
EX3-1	7	Unperformed	3	7.5	5	4.5	Sinusoidal	—	250	0.5	0.95	60
EX3-2	8	Unperformed	3	7.5	5	4.5	Sinusoidal	—	250	0.5	0.95	60
EX3-3	8	Unperformed	3	7.5	3	4.5	Sinusoidal	—	250	0.5	0.95	60
EX3-4	8	Unperformed	3	7.5	7	4.5	Sinusoidal	—	250	0.5	0.95	60
EX3-5	8	Unperformed	3	7.5	5	4.5	Trapezoidal	2.0	250	0.5	0.95	60

[0404]

TABLE 2-3

Second etching Amount	Second electrochemical graining					
	of aluminum dissolved (g/m ²)	Hydrochloric acid concentration (g/L)	Nitric acid concentration (g/L)	Aluminum ion concentration (g/L)	Waveform	Current rise time (msec)
EX1-1	0.5	7.5	0	5	Trapezoidal	0.8
EX1-2	0.5	7.5	0	5	Trapezoidal	0.8
EX1-3	0.5	7.5	0	5	Trapezoidal	0.8
EX1-4	0.5	7.5	0	5	Trapezoidal	0.8
EX1-5	0.5	7.5	0	5	Trapezoidal	0.8
EX1-6	0.5	7.5	0	5	Trapezoidal	0.8
EX1-7	0.5	7.5	0	5	Trapezoidal	0.8
EX1-8	0.5	7.5	0	5	Trapezoidal	0.8
EX1-9	0.5	7.5	0	5	Sinusoidal	0.8
EX1-10	0.5	7.5	0	5	Trapezoidal	0.8
EX1-11	0.5	7.5	0	5	Trapezoidal	0.8
EX1-12	0.5	7.5	0	5	Trapezoidal	0.8
EX1-13	0.2	7.5	0	5	Trapezoidal	0.8
EX1-14	1.0	7.5	0	5	Trapezoidal	0.8
EX1-15	1.5	7.5	0	5	Trapezoidal	0.8
EX1-16	3.0	7.5	0	5	Trapezoidal	0.8
EX1-17	0.5	7.5	0	5	Trapezoidal	0.8
EX1-18	0.5	7.5	0	5	Trapezoidal	0.8
EX1-19	0.5	7.5	0	5	Trapezoidal	0.8
EX1-20	0.5	7.5	1	5	Trapezoidal	0.8

TABLE 2-3-continued

		Second electrochemical			Third etching Amount of	Printing performance			
		graining			aluminum dissolved (g/m ²)	Cleaner			
		Duty ratio	Current ratio	Frequency (Hz)		Press life	press life	Scumming resistance	Shininess
EX1-1	0.5	0.95	60	0.1	A	A	A	A	
EX1-2	0.5	0.95	60	0.1	A	A	A	A	
EX1-3	0.5	0.95	60	0.1	A	A	A	A	
EX1-4	0.5	0.95	60	0.1	A	A	A	A	
EX1-5	0.5	0.95	60	0.1	A	A	A	A	
EX1-6	0.5	0.95	60	0.05	A	A	A-B	A	
EX1-7	0.5	0.95	60	0.2	A-B	A-B	A	A	
EX1-8	0.5	0.95	60	0.1	A	A	A	A	
EX1-9	0.5	1.00	60	0.1	A	A	A	A	
EX1-10	0.5	0.95	60	0.1	A	A	A	A	
EX1-11	0.5	0.95	60	0.1	A	A	A	A	
EX1-12	0.5	0.95	60	0.1	A	A	A	A	
EX1-13	0.5	0.95	60	0.1	A	A	A	A	
EX1-14	0.5	0.95	60	0.1	A	A	A	A	
EX1-15	0.5	0.95	60	0.1	A-B	A-B	A	A	
EX1-16	0.5	0.95	60	0.1	B	B	A	A	
EX1-17	0.5	0.95	60	0.1	A	A	A	A	
EX1-18	0.5	0.95	60	0.1	A	A	A	A	
EX1-19	0.5	0.95	60	0.1	A	A	A	A	
EX1-20	0.5	0.95	60	0.1	A	A	A	A	

[0405]

TABLE 2-4

	Second etching Amount of aluminum dissolved (g/m ²)	Second electrochemical graining				Current rise time (msec)	Amount of electricity (C/dm ²)
		Hydrochloric acid concentration (g/L)	Nitric acid concentration (g/L)	Aluminum ion concentration (g/L)	Waveform		
EX1-21	0.5	7.5	3	5	Trapezoidal	0.8	65
EX1-22	0.5	7.5	5	5	Trapezoidal	0.8	65
EX1-23	0.5	7.5	8	5	Trapezoidal	0.8	65
EX1-24	0.5	7.5	0	5	Sinusoidal	0.8	65
EX1-25	0.5	7.5	5	5	Sinusoidal	0.8	65
EX1-26	0.5	7.5	5	5	Sinusoidal	0.8	65
EX1-27	0.5	7.5	5	5	Trapezoidal	0.8	65
EX1-28	0.5	7.5	5	5	Trapezoidal	0.8	65
EX1-29	0.5	7.5	5	5	Trapezoidal	0.8	65
EX1-30	0.5	7.5	0	5	Trapezoidal	0.8	65
EX1-31	0.5	7.5	5	5	Sinusoidal	0.8	65
EX1-32	0.5	7.5	5	5	Trapezoidal	0.8	65
EX1-33	0.5	7.5	5	5	Trapezoidal	16.0	65
EX1-34	0.5	7.5	5	5	Sinusoidal	16.0	65
EX1-35	0.5	7.5	5	5	Triangular	16.0	65
EX2-1	0.5	7.5	5	5	Trapezoidal	0.8	65
EX2-2	0.5	7.5	0	5	Trapezoidal	0.8	65
EX2-3	0.5	7.5	5	5	Sinusoidal	0.8	65
CE1	—	—	—	—	—	—	—

TABLE 2-4-continued

		Second electrochemical			Third etching Amount of	Printing performance			
		graining			aluminum	Cleaner			
		Duty ratio	Current ratio	Frequency (Hz)		dissolved (g/m ²)	Press life	press life	Scumming resistance
EX1-21	0.5	0.95	60	0.1	A	A	A	A	
EX1-22	0.5	0.95	60	0.1	A	A	A	A	
EX1-23	0.5	0.95	60	0.1	A	A	A	A	
EX1-24	0.5	0.95	60	0.1	A	A	A	A	
EX1-25	0.5	0.95	60	0.1	A	A	A	A	
EX1-26	0.5	0.95	50	0.1	A	A	A	A	
EX1-27	0.5	0.95	60	0.1	A	A	A	A	
EX1-28	0.5	0.95	60	0.1	A-B	A	A	B	
EX1-29	0.5	0.95	60	0.1	A-B	A	A	B	
EX1-30	0.5	0.95	60	0.1	A-B	A	A	B	
EX1-31	0.5	0.95	60	0.1	A-B	A	A	B	
EX1-32	0.5	0.95	60	0.1	A-B	A	A	B	
EX1-33	0.5	0.95	30	0.1	A-B	A	A	B	
EX1-34	0.5	0.95	30	0.1	A-B	A	A	B	
EX1-35	0.5	0.95	30	0.1	A-B	A	A	B	
EX2-1	0.5	0.95	60	0.1	A	A	A	A	
EX2-2	0.5	0.95	60	0.1	A	A	A	A	
EX2-3	0.5	0.95	60	0.1	A	A	A	A	
CE1	—	—	—	0.1	C	B	C	A	

[0406]

TABLE 2-5

	Second etching Amount	Second electrochemical graining						
	of aluminum dissolved (g/m ²)	Hydrochloric acid concentration (g/L)	Nitric acid concentration (g/L)	Aluminum ion concentration (g/L)	Waveform	Current rise time (msec)	Amount of electricity (C/dm ²)	
EX3-1	0.8	7.5	0	4.5	Trapezoidal	1.0	65	
EX3-2	0.8	7.5	0	4.5	Trapezoidal	0.8	65	
EX3-3	0.8	7.5	0	4.5	Trapezoidal	0.8	65	
EX3-4	0.8	7.5	0	4.5	Trapezoidal	1.0	65	
EX3-5	0.8	7.5	0	4.5	Trapezoidal	2.0	65	

	Second electrochemical				Third etching Amount of	Printing performance			
	graining			aluminum dissolved (g/m ²)	Cleaner				
	Duty ratio	Current ratio	Frequency (Hz)		Press life	press life	Scumming resistance	Shininess	
EX3-1	0.5	0.95	60	0.15	A	A	A	B	
EX3-2	0.5	0.95	60	0.15	A	A	A	A	
EX3-3	0.5	0.95	60	0.15	A	A	A	A	
EX3-4	0.5	0.95	60	0.15	A	A	A	A	
EX3-5	0.5	0.95	60	0.15	A	A	A	A	

Note:

EX: Example

CE: Comparative Example

What is claimed is:

1. A method of manufacturing a lithographic printing plate support comprising the step of:

subjecting an aluminum plate at least to a first electrochemical graining treatment in which a first alternating current is passed through the aluminum plate in a first aqueous solution containing hydrochloric acid and nitric acid and a second electrochemical graining treatment in which a second alternating current is passed through the aluminum plate in a second aqueous solution containing hydrochloric acid in this order to obtain the lithographic printing plate support.

2. The method according to claim 1, wherein the aluminum plate has a pattern of recessed and protruded portions on a surface thereof.

3. The method according to claim 1, wherein the first alternating current is passed through the aluminum plate in the first electrochemical graining treatment so that a total amount of electricity when the aluminum plate serves as an anode is 100 to 300 C/dm².

4. The method according to claim 1, wherein the second alternating current is passed through the aluminum plate in the second electrochemical graining treatment so that a total amount of electricity when the aluminum plate serves as an anode is 10 to 300 C/dm².

5. The method according to claim 1, wherein the first aqueous solution used in the first electrochemical graining treatment has a hydrochloric acid concentration of 3 to 30 g/L and a nitric acid concentration of 0.5 to 15 g/L.

* * * * *