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(54) **Support for lithographic printing plate and presensitized plate**

(57) There is provided a support for a lithographic printing plate which has a scratch-resistant coating that is a porous layer of specifically high adiathermancy on a surface of a metal base plate subjected to acid or alkali treatment, and which is excellent in all of sensitivity, scum resistance and press life and also excellent in abrasion resistance since adhesion between the porous layer and the plate is excellent.

EP 1 477 321 A1

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a support for a lithographic printing plate and a presensitized plate. More particularly, the present invention relates to a support for a lithographic printing plate and a presensitized plate which have a porous layer with specially high adiathermancy, are capable of plate making by scanning exposure based on a digital signal, have scratch resistance, excellent sensitivity, scum resistance and press life, and are excellent in abrasion resistance because the adhesion between the porous layer and a base plate is excellent.

[0002] In the field of lithography, a metal base plate is widely used as the base of a support for a lithographic printing plate used for a presensitized plate to manufacture a lithographic printing plate. It is known that aluminum, above all, produces an anodized coating in such a manner that aluminum is allowed to be an anode in an acid solution and a direct current is applied to flow in the aluminum. Aluminum is capable of being subjected to the treatment generally known as alumite treatment and has various advantages such as lightweight and low price. If the alumite treatment is performed on the surface of aluminum, an alumina anodized coating has the following advantages in comparison with metal aluminum. The alumina anodized coating has high acid resistance and hardness. In the alumina anodized coating, a number of fine holes called pores are regularly produced in a coating structure, and a surface area is largely increased by BET process (gas adsorption process). Accordingly, the alumite treatment can improve the hydrophilicity of a support for a lithographic printing plate and can achieve improvements such as enhancement in adhesion when a coated film is formed. This allows an aluminum plate with the alumina anodized coating to have an advantage that both scum resistance (which means "fouling resistance" in the present invention) and press life can be achieved when the aluminum plate is processed into a lithographic printing plate.

[0003] In addition, in recent years, there has been noted a so-called heat mode-type CTP presensitized plate (hereinafter also referred to simply as "a heat mode-type presensitized plate") in which an image can be formed by exposure in a near-infrared to infrared area, and particularly plate making can be directly performed from digital data of a computer or the like by recording an image while utilizing heat generated when light is irradiated using a laser having a light emitting area in the near-infrared to infrared area.

[0004] In the presensitized plate, an irradiated laser beam for depicting an image is converted into heat by a photothermal converting material or the like contained in a photosensitive layer, and the solubility of the photosensitive layer to a developer is changed by the generated heat. Moreover, the photosensitive layer is thermally decomposed by the generated heat or subjected to explosive expansion removal (abrasion) by abrupt heating. If a metal base plate such as an aluminum plate is used as a support for the heat mode-type presensitized plate as described above, since the thermal conductivity of the metal base plate is high, the generated heat is rapidly radiated to the support side and thus lost. This is one of the causes to deteriorate the sensitivity of the presensitized plate. Conversely, if the adiathermancy of the surface of a support for a lithographic printing plate can be improved to minimize the radiation phenomenon of the heat generated in the photosensitive layer, it is expected that the sensitivity of the presensitized plate can be improved.

[0005] On the other hand, it is the present situation that, although a method for highly improving the sensitivity using, as a support, an organic material of low-thermal conductivity such as PET is also attempted, the organic material can not be used for a high-performance printing such as color printing and high-definition printing because the hydrophilicity is low as compared with that of a metal material and therefore moisture is absorbed while printing to deteriorate dimension accuracy.

[0006] Therefore, for a support for use in a heat mode-type presensitized plate, it is required that the low adiathermancy attributable to the high thermal conductivity of a metal base plate is improved while making use of the facility of various surface treatments of the metal base plate and the excellent points such as hydrophilicity and dimension accuracy stability.

[0007] On the other hand, although an anodic oxide coating formed on a support for a lithographic printing plate is a coating of low thermal conductivity, in place of this anodic oxide coating, there has been proposed, for example, a hydrophilic layer for a lithographic printing plate characterized by having a hydrophilic layer containing alumina (aluminum oxide) particles and by being formed through a treatment of the hydrophilic layer in a solution containing silicic acid (see JP 2000-169758 A). In addition, there has been proposed a method of manufacturing a photosensitive substance including a process where slurry containing at least inorganic nonmetal particles and monobasic phosphate is coated on a base plate having an aluminum surface and a hydrophilic ceramic layer is formed by sufficiently dehydrating and drying the coated layer at a temperature of at least 230°C or higher, and a process where an organic photosensitive layer is formed on the hydrophilic ceramic layer (see US 4,542,089).

[0008] However, the hydrophilic layer for a lithographic printing plate is a layer formed by making use of the self-film-forming property of alumina sol, and the strength of the layer is yet weak. For this reason, the hydrophilic layer and a support for a lithographic printing plate provided with the hydrophilic layer are poor in scratch resistance. In addition,

they may be poor in press life when processed into a lithographic printing plate. On the other hand, a lithographic printing plate provided with the hydrophilic layer may not obtain a sufficiently satisfactory scum resistance. In addition, a drying process is performed on the hydrophilic ceramic layer at a high temperature of more than 230°C and drying equipment capable of performing such high temperature drying is generally expensive. Further, if an aluminum plate provided with the hydrophilic ceramic layer is dried at a very high temperature (for example, 260°C or higher), the aluminum plate is softened, and the excellent dimension accuracy stability or the like that the aluminum plate has is lost, which may cause a defect that the plate is extended particularly at the time of printing, and the plate and an image are deviated.

SUMMARY OF THE INVENTION

[0009] It is an object of the present invention to provide a support for a lithographic printing plate which overcome the above-mentioned disadvantages of technology, has a scratch-resistant coating that is a porous layer with specifically high adiathermancy, is excellent in sensitivity when processed into a presensitized plate and excellent in scum resistance and press life when processed into a lithographic printing plate, and is excellent in abrasion resistance because the adhesion between the porous layer and a base plate is excellent, and to provide a presensitized plate using the same.

[0010] In the present invention, sensitivity means the sensitivity when a presensitized plate is manufactured, and scum resistance and press life mean the scum resistance and press life when a lithographic printing plate is manufactured.

[0011] The present inventors have intensively studied and found that if particles of a metal oxide are bonded onto a base plate by a compound containing a metal atom and a phosphorus atom, a porous layer in which a suitable quantity of the air is taken can be formed and the porous layer has excellent adiathermancy and high film strength. The inventors have also found that if a specified pretreatment is performed on a metal base plate, the adhesion between the porous layer and the base plate is improved and a support for a lithographic printing plate excellent in abrasion resistance can be obtained, exhibiting sensitivity, excellent scum resistance and press life.

[0012] That is to say, the present invention is realized based on the above-mentioned findings and provides the following (1) to (10).

(1) A support for a lithographic printing plate having a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom on a surface of a metal base plate subjected to acid or alkali treatment.

(2) A method of manufacturing a support for a lithographic printing plate, characterized by performing acid or alkali treatment on a surface of a metal base plate and providing thereon a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom.

(3) A support for a lithographic printing plate having a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom on a surface of a metal base plate subjected to acid or alkali treatment and/or anodizing treatment.

(4) A method of manufacturing a support for a lithographic printing plate, characterized by performing beforehand acid or alkali treatment and/or anodizing treatment on a surface of a metal base plate and providing thereon a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom.

(5) The support for a lithographic printing plate or the method of manufacturing the same according to any one of the items (1) to (4), wherein the metal oxide is at least one kind of metal oxide or composite oxide selected from the group consisting of silicon, magnesium, zirconium and titanium.

(6) The method of manufacturing the support for a lithographic printing plate according to any one of the items (2), (4) and (5), wherein a sealing layer is further provided on the porous layer.

(7) The support for a lithographic printing plate according to any one of the items (1), (3) and (5), further having a sealing layer on the porous layer.

(8) The support for a lithographic printing plate or the method of manufacturing the same according to the item (1) or (7), wherein a porosity of the porous layer is 20% or higher and/or a porosity of the sealing layer is less than the porosity of the porous layer.

(9) The support for a lithographic printing plate or the method of manufacturing the same according to any one of the items (1) to (8), wherein a film thickness of the porous layer is 0.5 to 20 μm and/or a film thickness of the sealing layer is 0.01 to 0.5 μm.

(10) A presensitized plate having an image recording layer on the support for a lithographic printing layer or the support obtained by the method of manufacturing the same according to any one of the items (1) to (9).

BRIEF DESCRIPTION OF THE DRAWING

[0013]

Fig. 1 is a schematic diagram of the anodizing treatment device used for anodizing of a support for a lithographic printing plate of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Hereinafter, detailed description will be given of a support for a lithographic printing plate and a presensitized plate of the present invention.

[Support for Lithographic Printing Plate]

(Pretreatment)

[0015] For the support for a lithographic printing plate of the present invention, pretreatment of <acid or alkali treatment> and/or <anodizing treatment> to be described below are performed on an undermentioned base plate. Each treatment may be performed a plurality of times and an arbitrary combination thereof may be performed.

[0016] By being subjected to the pretreatment, the support for a lithographic printing plate of the present invention is excellent in adhesion between a porous layer and the base plate, which will be described later. Therefore, the characteristics of the porous layer can be effectively utilized, and the support for a lithographic printing plate is further excellent in abrasion resistance.

[0017] In addition, before the pretreatment according to the present invention, degreasing treatment may be performed, if required, in which rust preventive oil is removed in advance from the surface of the metal base plate by use of a solvent of alcohol, methyl ethyl ketone or the like.

<Acid or Alkali Treatment>

(Alkali Treatment)

[0018] Alkali treatment is a treatment which dissolves a surface layer of the metal base plate by bringing the metal base plate into contact with an alkali solution.

[0019] Since a naturally oxidized coating and the like exist on the surface layer of the metal base plate, the alkali treatment is performed to dissolve the naturally oxidized coating and the like and to improve the adhesion to a porous layer to be provided on an upper layer of the metal base plate.

[0020] The dissolved amount of an alkali is preferably in a range of 0.5 to 10g/m^2, more preferably 1 to 5g/m^2, and most preferably 1 to 3g/m^2.

[0021] If the dissolved amount is too small, the adhesion between the base plate and the porous layer may not be improved. In addition, scum may be worsened during printing. On the other hand, if the dissolved amount exceeds 20g/m^2, it may not be economical.

[0022] The alkalis used for the alkali solution include, for example, caustic alkalis and alkali metal salts. More specifically, the caustic alkalis include, for example, caustic soda and caustic potash. The alkali metal salts include, for example, alkali metal silicates such as sodium metasilicate, sodium silicate, potassium metasilicate and potassium silicate; alkali metal carbonates such as sodium carbonate and potassium carbonate; alkali metal aluminates such as sodium aluminate and potassium aluminate; alkali metal aldonates such as sodium gluconate and potassium gluconate; and alkali metal hydrogenphosphates such as sodium secondary phosphate, potassium secondary phosphate, sodium tertiary phosphate and potassium tertiary phosphate. Above all, preferable are a caustic alkali solution and a solution containing both a caustic alkali and an alkali metal aluminate, from the viewpoint of high etching rate and low price. An aqueous solution of caustic soda is particularly preferable.

[0023] Although the concentration of the alkali solution can be determined depending on a dissolved amount of an alkali required for a metal base plate, the concentration of the alkali solution is preferably 1 to 50 mass%, more preferably 10 to 35 mass%. If metal-base-plate ions such as aluminum ions are dissolved in the alkali solution, the concentration of the ion is preferably 0.01 to 10 mass%, more preferably 3 to 8 mass%. The temperature of the alkali solution is preferably 20 to 90°C. The treatment time is preferably 1 to 20 seconds.

[0024] Methods of bringing the metal base plate such as an aluminum plate into contact with the alkali solution include, for example, a method of allowing the aluminum plate to pass through a bath containing the alkali solution, a method of dipping the aluminum plate into a bath containing the alkali solution, and a method of spraying the alkali

solution onto the surface of the aluminum plate.

(Acid Treatment)

[0025] Acid treatment (pickling treatment) is performed on the surface of the metal base plate to remove a naturally oxidized layer and scum therefrom, and the adhesion to a porous layer to be provided on an upper layer of the metal base plate is improved. The alkali treatment described above and the acid treatment may be performed independently or in combination. Each treatment may be performed a plurality of times and an arbitrary combination thereof may be performed.

[0026] Acids to be used include, for example, nitric acid, sulfuric acid, phosphoric acid, chromic acid, hydrofluoric acid and fluoroboric acid.

[0027] The acid treatment is performed, for example, by bringing the metal base plate such as an aluminum plate into contact with an acid solution, such as hydrochloric acid, nitric acid or sulfuric acid, with an concentration of 0.5 to 30 mass% (containing 0.01 to 5 mass% of metal ions such as aluminum ions). Methods of bringing the aluminum plate into contact with the acid solution include, for example, a method of allowing the aluminum plate to pass through a bath containing the acid solution, a method of dipping the aluminum plate into a bath containing the acid solution, and a method of spraying the acid solution onto the surface of the aluminum plate.

[0028] In the acid treatment, as the acid solution, waste water of an aqueous solution containing nitric acid or hydrochloric acid discharged in publicly known electrolytic graining treatment or waste water of an aqueous solution containing sulfuric acid discharged in undermentioned anodizing treatment can be used.

[0029] The temperature of the solution for use in the acid treatment is preferably 50 to 90°C. In addition, the treatment time is preferably 1 to 180 seconds, more preferably 2 to 30 seconds. Metal base plate components such as aluminum or an aluminum alloy may be dissolved in the acid solution for use in the acid treatment.

<Anodizing Treatment>

[0030] For the pretreatment of the metal base plate such as an aluminum plate for use in the present invention, the <acid or alkali treatment> may be performed by itself, or <anodizing treatment> to be described below may be performed by itself. In any case, a support for a lithographic printing plate having good adhesion (press life, scratch resistance) can be obtained. Each treatment may be performed a plurality of times, or both the treatments may be performed in combination. It is considered that the adhesion is increased in such a manner that alumina formed by an anodic oxide coating reacts with a phosphorus component in the undermentioned porous layer. The anodizing treatment can be performed by a method conventionally conducted in this field. In this case, for example, an anodic oxide coating can be formed by allowing a current to flow in an aluminum plate while using it as an anode in a solution with a sulfuric acid concentration of 50 to 300g/L and an aluminum concentration of 5 mass% or less. As the solution for use in the anodizing treatment, sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid, benzenesulfonic acid, amidosulfonic acid or the like can be used by itself or in a combination of two kinds or more thereof.

[0031] In this case, it is permissible that a component generally contained in at least a metal base plate such as aluminum, an electrode, city water, ground water or the like, is contained in the electrolytic solution. It is further permissible that second and third components are added thereto. The second and third components described here include, for example, metal ions such as Na, K, Mg, Li, Ca, Ti, Al, V, Cr, Mn, Fe, Co, Ni, Cu and Zn; cation such as ammonium ion; and anions such as nitrate ion, carbonate ion, chloride ion, phosphate ion, fluoride ion, sulfite ion, titanate ion, silicate, and borate ion, and they may be contained at a concentration of 0 to about 10000 ppm.

[0032] Although the conditions of the anodizing treatment cannot be flatly determined since they largely vary depending on an electrolytic solution to be used, it is generally appropriate that the concentration of the electrolytic solution is 1 to 80 mass%, the temperature of a solution is 5 to 70°C, current density is 0.5 to 60A/dm^2, voltage is 1 to 100V, and the time of electrolysis is 1 second to 50 minutes. These conditions are controlled so as to obtain a desired quantity of the anodic oxide coating.

[0033] In addition, it is also possible to use a method as described in any of the 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, JP 5-195291 A, and the like.

[0034] Above all, it is preferable to use a sulfuric acid solution, as the electrolytic solution, as described in JP 54-12853 A and JP 48-45303 A. The concentration of sulfuric acid in the electrolytic solution is preferably 10 to 300g/L (1 to 30 mass%), more preferably 50 to 200g/L (5 to 20 mass%). The concentration of aluminum ion is preferably 1 to 25g/L (0.1 to 2.5 mass%), more preferably 2 to 10g/L (0.2 to 1 mass%). Such an electrolytic solution can be prepared, for example, by adding aluminum sulfate or the like to dilute sulfuric acid with a sulfuric acid concentration of 50 to 200g/L.

[0035] The temperature of the electrolytic solution is preferably 25 to 55°C, more preferably 30 to 50°C.

[0036] If the anodizing treatment is performed in an electrolytic solution containing sulfuric acid, a direct current may be applied between the aluminum plate and a counter electrode, or an alternating current may be applied therebetween.

[0037] If a direct current is applied to the aluminum plate, the current density is preferably 1 to 60 A/dm^2, more preferably 3 to 40 A/dm^2.

[0038] If the anodizing treatment is continuously performed, it is preferable that, in order to prevent so-called "burning" caused by a current concentrating on a part of the aluminum plate, a current is allowed to flow at a low current density of 5 to 10 A/dm^2 at the initial stage of the anodizing treatment and the current density is increased to 30 to 50 A/dm^2 or higher as the anodizing treatment progresses.

[0039] If the anodizing treatment is continuously performed, it is preferable that the treatment is performed by a submerged power supply system in which electric power is supplied to the aluminum plate through the electrolytic solution.

[0040] A porous coating having a number of holes called pores (micro pores) can be obtained by performing the anodizing treatment under the conditions as described above. The average pore size is generally about 5 to 50 nm and the average pore density is about 300 to 800 pieces/μm^2.

[0041] The quantity of the anodic oxide coating is preferably 0.3 to 15 μm. If it is less than 1g/m^2, the plate is liable to be scratched. On the other hand, if it exceeds 5g/m^2, the manufacture thereof requires a huge amount of electric power, resulting in a disadvantage in terms of costs. The quantity of the anodic oxide coating is more preferably 1.5 to 4 g/m^2. In addition, it is preferable that the anodizing treatment is performed so that a difference in quantity of the anodic oxide coating between the central part and the vicinity of the edge of the aluminum plate is less than 1g/m^2.

[0042] As an electrolyzer for use in the anodizing treatment, it is possible to use one described in any of the JP 48-26638 A, JP 47-18739 A, JP 58-24517 B, JP 2001-11698 A and the like.

[0043] Above all, a device shown in Fig. 1 is suitably used. Fig. 1 is a schematic diagram showing one example of the device which performs anodizing treatment on the surface of the aluminum plate.

[0044] In an anodizing treatment device 410 shown in Fig. 1, a power supplying bath 412 is disposed on the upstream side in the traveling direction of an aluminum plate 416 and an anodizing treatment bath 414 is disposed on the downstream side therein in order to apply a current to the aluminum plate 416 through the electrolytic solution. The aluminum plate 416 is conveyed, as shown by the arrows in Fig. 1, by use of pass rollers 422 and 428. In the power supplying bath 412 into which the aluminum plate 416 is first introduced, an anode 420 connected with the positive electrode of a DC power supply 434 is disposed and the aluminum plate 416 serves as a cathode. Therefore, a cathodic reaction occurs in the aluminum plate 416.

[0045] In the anodizing treatment bath 414 into which the aluminum plate 416 is subsequently introduced, a cathode 430 connected with the negative electrode of the DC power supply 434 is disposed and the aluminum plate 416 becomes an anode. Therefore, an anodic reaction occurs in the aluminum plate 416, and an anodic oxide coating is thus formed on the surface of the aluminum plate 416.

[0046] It is preferable that the distance between the aluminum plate 416 and the cathode 430 is 50 to 200 mm. Aluminum is used for the cathode 430. In order to allow hydrogen gas which is produced by the anodic reaction to be easily discharged from the system, it is preferable that the cathode 430 is not an electrode which has a large area but is a plurality of separated electrodes disposed along the traveling direction of the aluminum plate 416.

[0047] As shown in Fig. 1, it is preferable that a bath, called an intermediate bath 413, which does not store an electrolytic solution is provided between the power supplying bath 412 and the anodizing treatment bath 414. The provision of the intermediate bath 413 can suppress a current from bypassing from the anode 420 to the cathode 430 without flowing through the aluminum plate 416. It is preferable that a bypass current is minimized as much as possible by disposing a nip roller 424 in the intermediate bath 413 to remove the solution from the aluminum plate 416. The electrolytic solution produced by the removal of the solution is drained from a discharge port 442 to the outside of the anodizing treatment device 410.

[0048] In order to reduce the loss of voltage, an electrolytic solution 418 stored in the power supplying bath 412 is to have a higher temperature and/or a higher concentration than those of an electrolytic solution 426 stored in the anodizing treatment bath 414. In addition, the compositions, temperatures and the like of the electrolytic solutions 418 and 426 are determined depending on the formation efficiency of the anodic oxide coating, the shapes of the micro pores in the anodic oxide coating, the hardness of the anodic oxide coating, the voltage, the costs of the electrolytic solutions, and the like.

[0049] The respective electrolytic solutions are spouted and supplied into the power supplying bath 412 and the anodizing treatment bath 414 from solution supplying nozzles 436 and 438, respectively. In order to make the distribution of the electrolytic solutions constant and prevent a current from locally concentrating on the aluminum plate 416 in the anodizing treatment bath 414, the solution supplying nozzles 436 and 438 are provided with slits and are of a structure which keeps a constant spouted solution flow in a width direction.

[0050] In the anodizing treatment bath 414, a baffle 440 is provided on the opposite side to the anode 430 relative to the aluminum plate 416 and suppresses a current from flowing to a side opposite to the surface of the aluminum

plate 416 on which the anodic oxide coating is desired to be formed. It is preferable that the distance between the aluminum plate 416 and the baffle 440 is 5 to 30 mm. It is preferable that a plurality of the DC power supplies 434 are used and the positive electrodes thereof are connected to one line in common for use. With this configuration, it is possible to control the current distribution in the anodizing treatment bath 414.

[0051] Since the anodic oxide coating has a low thermal conductivity of its own, the anodic oxide coating can further lower the thermal conductivity of the support for a lithographic printing plate and can also enhance the adhesion between the metal base plate and the porous layer. Further, if required, the thickness of the anodic oxide coating may be increased, and the porosity of the coating may be increased in such a manner that the plate is dipped into an acid or alkali aqueous solution after the formation of the anodic oxide coating and the size of the pores existing in the coating is enlarged.

<Porous Layer>

[0052] The support for a lithographic printing plate of the present invention is a support for a lithographic printing plate having a porous layer (hereinafter referred to as "porous layer of the present invention") where particles of a metal oxide are bonded onto the above-described base plate after the pretreatment by a compound containing a metal atom and a phosphorus atom.

[0053] It is considered that the porous layer of the present invention provided on the base plate is a layer where a number of metal oxide particles are bonded through a compound containing a metal atom and a phosphorus atom. More specifically, the porous layer is a layer where the surface of each metal oxide particle is partially, preferably entirely, covered with the compound containing a metal atom and a phosphorus atom; the compound containing the metal atom and phosphorus atom is solidified; and a plurality of the metal oxide particles covered with the solidified compound in an agglutinated condition are bonded through the compound containing the metal atom and phosphorus atom.

[0054] Voids are formed between the plurality of bonded particles. These voids can take air in, and the porosity of the porous layer is increased, improving the adiathermancy. In addition, since the particles are bonded through the compound containing a metal atom and a phosphorus atom or the like, the layer strength of the porous layer is high, and the porous layer is excellent in scratch resistance and also in press life.

[0055] The bonded metal oxide particles which form the porous layer are particles of a metal oxide which are residual after part of (the surface of) the metal oxide to be described later reacts with a phosphate, and it is considered that the particles are residual particularly without largely reducing their particle sizes.

[0056] That is to say, one of the characteristic features of the present invention is that the surfaces of the particles of a metal oxide are dissolved (the entire of each particle is not dissolved).

[0057] As a method of dissolving the surfaces, it is possible to cite, for example, a method of setting conditions (temperature, pH and the like) under which the pH of a coating solution is lowered and the temperature thereof is increased while the coating solution is coated or dried and thus a reaction occurs, although the conditions are such that a reaction of the metal oxide particles and a phosphate is difficult to occur in the undermentioned condition of the coating solution (slurry).

[0058] Specifically, it is possible to cite a method of specifying a drying temperature in the drying process to be described later (preferably a method of further specifying drying duration), a method of specifying a quantity of a metal oxide to react with a phosphate to be described later, a method of adding a catalyst, a reaction accelerator or the like, a method of suitably combining these methods, and the like.

[0059] The average size or the like of the metal oxide particles to form the porous layer is not particularly limited and varies depending on the sizes of the particles of a metal oxide to be used for the coating solution to be described later.

[0060] In addition, the metal oxide and the particles are basically the same as those explained in the coating solution to be described later.

[0061] The compound containing a metal atom and a phosphorus atom to form the porous layer is a reaction product of a phosphate to be described later and a metal oxide, a reaction product of the phosphate and a reaction accelerator to be described later, or the like, and functions as a bonding agent which bonds the particles of the metal oxide to each other.

[0062] Although the compound cannot be flatly determined since it varies depending on a metal oxide to be used, a phosphate to be used, and a reaction accelerator to be arbitrarily used, the compound may contain another atom, for example, an oxygen atom or the like. As the compound, it is possible to cite, for example, $Mg_2P_2O_7$, $Mg_3(PO)_4$, and the like if MgO is used as the metal oxide. Other examples are those described in "Chemistry," Japan Chemical Association, Vol. 31, No. 11, pp. 895 to 897.

[0063] The compound containing a metal atom and a phosphorus atom is not limited to the above-mentioned compounds and may be "a bonding group containing a metal atom and a phosphorus atom" which bonds particles of a metal oxide to each other. The bonding group may be of high molecular weight.

[0064] The compositions of the compound containing a metal atom and a phosphorus atom and of the bonding group containing a metal atom and a phosphorus atom are not particularly limited.

[0065] In the formation of the porous layer of the present invention, a reaction accelerator containing a metal atom different from that of the metal oxide, or the like can be used as described later. Therefore, a metal atom in the compound containing the metal atom and a phosphorus atom may be a metal atom derived from the reaction accelerator.

[0066] It is preferable that a metal atom in the compound containing the metal atom and a phosphorus atom is of the same kind as a metal atom of a metal oxide, and it is more preferable that the metal atom is a metal atom derived from the metal oxide.

[0067] In the porous layer, the abundance ratio of the metal oxide particles and the compound containing a metal atom and a phosphorus atom, or the like is not particularly limited. The quantity of the compound containing a metal atom and a phosphorus atom is more than a quantity at which the metal oxide particles can be bonded at least and is less than a quantity at which the voids between the particles are completely filled. For example, the quantity of the compound is determined depending on the composition of the coating solution to be described later.

[0068] The porous layer of the present invention may contain another compound besides the metal oxide particles and the compound containing a metal atom and a phosphorus atom described above.

[0069] As the other compound, it is possible to cite, for example, a dispersant, a reaction accelerator and the like to be described later, as well as a reaction product of any of these compounds and the metal oxide or compound containing a metal atom and a phosphorus atom, and the like.

[0070] The porosity of the porous layer of the present invention is preferably 20% or higher, more preferably 40% or higher, and further preferably 45% or higher. If the porosity is set to 20% or higher, the porous layer can take a suitable quantity of air in, is therefore excellent in adiathermancy and is enhanced in sensitivity.

[0071] In addition, it is preferable that the porosity is set to 70% or less, more preferably to 60% or less, for the reason that the porous layer becomes excellent in press life while maintaining its high layer strength.

[0072] Concerning the measurement of the porosity of the porous layer, the porosity can be determined from the film thickness of the porous layer and the mass of the porous layer after dried, which will be described below.

[0073] Specifically, the density of the porous layer is first calculated by the following equation. For this purpose, the mass of the porous layer after dried is measured to determine the mass of the porous layer per unit area, and the film thickness of the porous layer is measured by a method to be described later.

$$\text{Density (g/cm}^3\text{)} = (\text{Mass of Layer per Unit Area/Film Thickness})$$

[0074] Next, the porosity of the porous layer can be calculated by the following equation based on the density calculated above:

$$\text{Porosity (\%)} = \{1 - (\text{Density of Porous Layer}/D)\} \times 100$$

where D is the density (g/cm^3) according to the Handbook of Chemistry, of a metal oxide to be used to form the porous layer.

[0075] The film thickness of the porous layer of the present invention is preferably 0.5 to 20 μm, more preferably 1 to 10 μm, and further preferably 3 to 7 μm. If the film thickness is 0.5 μm or more, the layer strength of the porous layer is high and the porous layer is excellent in scratch resistance and press life. In addition, the adiathermancy of the porous layer is high, and the porous layer is excellent in sensitivity.

[0076] Although the upper limit of the film thickness is set to 20 μm for the reason of costs because any further effect cannot be obtained, the upper limit may not be limited to this value and may be 20 μm or more.

[0077] Concerning a method of measuring the film thickness of the porous layer, a fracture face produced by bending a support for a lithographic printing plate provided with the porous layer is first observed and micrographed with an ultra high-resolution scanning electron microscope (for example, S-900 made by Hitachi, Ltd.). Note that the observation magnification is suitably adjusted depending on the film thickness and the like. Specifically, it is preferable that the magnification is 100 to 10,000 times.

[0078] Next, the thickness of the porous layer in the obtained image data (micrograph) is measured, and thus the film thickness of the porous layer can be determined by converting the measured value.

[0079] Note that the porous layer of the present invention may be one layer or a plurality of layers where two layers or more are superimposed.

[0080] If a plurality of layers are prepared, a porous layer is coated and dried, and thereafter another identical porous

layer may be superimposed thereon or a porous layer of a different composition may be superimposed thereon. The film thickness of each layer is not particularly limited, and the film thicknesses of the layers may be constant or different.

[0081] In order to form a plurality of layers, for example, a coating process where a coating solution is coated and a drying process where the coating solution is dried, which will be described later, may be alternately performed.

[0082] The porous layer can be formed on the base plate, for example, by a method including a coating process where a coating solution containing a granular metal oxide and a phosphate is coated onto the base plate and a drying process where the coating solution coated on the base plate is heated and dried at 180 to 500°C.

[0083] In other words, the support for a lithographic printing plate of the present invention is a support for a lithographic printing plate provided with a porous layer on a base plate, the porous layer being obtained in such a manner that a coating solution containing a granular metal oxide and a phosphate is coated on the base plate and the coating solution is dried at 180 to 500°C.

[0084] Although the detail of a reaction mechanism where the porous layer is formed is not understood, the mechanism is considered by the inventors as follows. The mechanism will be described, taking magnesia (MgO) as an example.

[0085] It is considered that, in the reaction of magnesia and phosphoric acid, the chemical reactions represented by the following formulas (1) and (2) occur, and particles of the metal oxide are bonded by $Mg_2P_2O_7$ or the like which is produced. It is also considered that if the coating solution is completely dried, $MgHP_4$ produced in the formula (1) may function as a bonding agent.

$$MgO+H_3PO_4 \xrightarrow{20℃} MgHPO_4+H_2O \qquad (1)$$

$$2MgHPO_4 \xrightarrow{200\sim300℃} Mg_2P_2O_7+H_2O \qquad (2)$$

[0086] That is to say, if the pH of the coating solution containing the granular metal oxide and the phosphate is within a preferable range to be described later, the surfaces of the metal oxide particles is slightly dissolved under the acid condition, and the metal oxide the surface of which is dissolved and the eluted metal oxide become likely to react with the phosphate. In addition, under the acid condition, the surface of the base plate also reacts with the phosphate and is activated.

[0087] After the coating solution is coated, and preferably in the drying process, water in the coating solution is removed, and the concentration of the phosphate is increased, and at the same time, the temperatures of the coating solution and the base plate rise. Then, the base plate, the metal oxide the surface of which is dissolved and the eluted metal oxide react with the phosphate to gradually produce a water-insoluble compound containing a metal atom and a phosphorus atom. This water-insoluble compound functions as a bonding agent which bonds particles of the metal oxide to each other. Thus, a porous layer in which a plurality of the metal oxide particles are bonded and a preferred quantity of air is taken is formed.

[0088] The porous layer bonded by the water-insoluble compound is excellent in adiathermancy because the preferred quantity of air is taken therein. Moreover, the layer strength of the porous layer is increased because the porous layer is bonded by the compound.

[0089] It is considered that, in such a mechanism, if a reaction accelerator is used, the reaction described above occurs at lower temperature, and $Mg_2P_2O_7$ or the like which functions as a bonding agent is more easily produced at lower temperature. This is particularly effective if an aluminum plate, which is disadvantageous in high temperature drying, is used as the base plate. The softening of the aluminum plate due to the high temperature mentioned above can be suppressed, and a lithographic printing plate having excellent characteristics can be obtained.

[0090] Incidentally, the detail of such a reaction of a phosphate and a metal oxide is described in "Chemistry," Japan Chemical Association, Vol. 31, No. 11, pp. 895 to 897.

[0091] Description will be given of the coating solution for use in the coating process where the coating solution containing the granular metal oxide and phosphate is coated onto the base plate.

[0092] The metal oxide contained in the coating solution used to form the porous layer of the present invention is not particularly limited as long as it is a metal oxide which reacts with the phosphate to be described later and forms a coating. It is possible to cite, for example, oxides of metals described in "Zhurnal Prikladnoi Khimii," Vol. 38, No.7, pp. 1466 to 1472 (July in 1965). Specifically, it is possible to cite oxides of Al, Si, Ti, Zr, Y, Nd, La, Mg, Ca, Sr, Ba, Cr, Co, Fe, Ni, Sn, Pb, Cu, Zn, Cd, Mn, and the like. Among these, preferable is an oxide or composite oxide of at least one kind of metal or more selected from the group consisting of Si, Mg, Zr, and Ti.

[0093] More specifically, as the metal oxide used to form the porous layer of the present invention, it is possible to

cite, for example, metal oxides such as SiO_2, TiO_2, Al_2O_3, ZrO_2, Y_2O_3, Nd_2O_3, La_2O_3, MgO CaO, SrO, BaO, MnO_2, CrO_2, CO_2O_3, Fe_2O_3, Mn_2O_3, NiO, FeO, MnO, SnO_2, PbO_2, CuO, ZnO, CdO, and the like. In addition, it is possible to cite, for example, mixed oxides of the metal oxides cited above, such as SiO_2/Al_2O_3, MgO/Al_2O_3, and the like.

[0094] Further, as the composite oxide, it is possible to cite, for example, $2SiO_2 \cdot 3Al_2O_3$ (mullite) and the like.

[0095] As the particles of the above-mentioned metal oxides, concretely, various commercial alumina particulates are available, such as AKP series, AKP-G series, HIT series, AM series (made by Sumitomo Chemical Co., Ltd.), Nano Tek series (generally called ultra-fine particles, made by C.I. Kasei Co., Ltd.).

[0096] More specifically, the followings can be cited.

[0097] It is possible to cite Al_2O_3 (AKP-50, average particle size: 0.3 μm, made by Sumitomo Chemical Co., Ltd.), SiO_2 (Towanalight FTB, average particle size: 12 μm, made by Towana Corporation; Silica sand SP-80, average particle size: 5.5 μm, made by San-ei Silica Co., Ltd.; SI-0010, average particle size: 10 μm, Reagent made by Soekawa Rikagaku Co., Ltd.; Commercial name: SO-C1, particle size: 0.2 to 0.3 μm, made by Admatechs Co., Ltd.), MgO (Ube Materials 2000A, average particle size: 0.2 μm, made by Ube Industries, Ltd.; MG-0076, average particle size: 2 mm, Reagent made by Soekawa Rikagaku Co., Ltd.), ZrO_2 (Commercial name: Spherical Silica Containing Zirconia, average particle size: 0.7 μm, made by Admatechs Co., Ltd.; Nano Tek series (generally called ultra-fine particles) ZrO_2, average particle size: 0.03 μm, made by C.I. Kasei Co., Ltd.; ZR-0049, average particle size: 8 μm, Reagent made by Soekawa Rikagaku Co., Ltd.), TiO_2 (Rutile, TI-0057, average particle size: 1 to 2 μm, Reagent made by Soekawa Rikagaku Co., Ltd.), SiO_2/Al_2O_3 (Nano Tek series (generally called ultra-fine particles) SiO_2/Al_2O_3, average particle size: 0.03 μm, made by C.I. Kasei Co., Ltd.), MgO/Al_2O_3 (Nano Tek series (generally called ultra-fine particles) MgO/Al_2O_3, average particle size: 0.05 μm, made by C.I. Kasei Co., Ltd.), $2SiO_2 \cdot 3Al_2O_3$ (mixed oxide mullite (powder), average particle size: 0.8 μm, made by KCM Corporation; AL-0111, average particle size: 5 μm, Reagent made by Soekawa Rikagaku Co., Ltd.; Commercial name: Alumina-Silica Composite Oxide, average particle size: 0.6 μm, made by Admatechs Co., Ltd.), and the like.

[0098] In addition, products, if they are generally commercially available, can be used with no particular restriction, besides those described above.

[0099] These particles are used after adjusting the average particle sizes by crushing or the like, as desired.

[0100] Other metal oxides may be also contained in addition to any of the metal oxides described above. As the other metal oxides, it is possible to cite, for example, oxides of metals or the like other than those exemplified above.

[0101] Although the content of a metal oxide used to form the porous layer of the present invention is not particularly limited, the content is preferably 10 to 100 mass% of the total metal oxides including the other metal oxides, more preferably 40 to 100 mass%.

[0102] In the present invention, the metal oxide is particulate in order that a preferred quantity of air is taken in to improve the adiathermancy. However, the metal oxide particles may be in any shape of a sphere, a polyhedron (for example, 20-polyhedron, 12-polyhedron and the like), a cube, a tetrahedron, a so-called confeito-shape (burr-like candy shape), a plate-shape, a needle-shape, and the like as long as the effects of the present invention are exerted. The sphere, polyhedron, cube, tetrahedron and confeito-shape are preferable for the reason that they are likely to become a sphere by reaction with the metal oxide or the compound containing a metal atom and a phosphorus atom, which will be described later, and are excellent in adiathemancy. The sphere shape is also preferable for the reason that it is easily procured and is excellent in adiathermancy.

[0103] In addition, the metal oxide particles may have a mixture of these shapes, and the shapes may be hollow shapes having these shapes.

[0104] Although the average particle size of the particles is not particularly limited, the average particle size is preferably 0.01 to 5 μm, more preferably 0.03 to 3 μm, and further preferably 0.03 to 1.5 μm. If the size is within this range, the layer strength is high and the porosity is easily controlled to the preferred range as described earlier.

[0105] In addition, if the adhesion to an image recording layer is insufficient or the like, in order to increase surface roughness, particles of two kinds or more of metal oxide having different average particle sizes may be mixed. In this case, the average particle size of particles of a first metal oxide is preferably 0.01 to 5 μm, more preferably 0.03 to 3 μm, and further preferably 0.03 to 1.5 μm. The average particle size of particles of a second metal oxide is preferably 2 to 50 times the average particle size of particles of the first metal oxide, more preferably 3 to 20 times, and further preferably 4 to 10 times.

[0106] The surface roughness can be controlled to desired roughness by using the second metal oxide particles having the larger average particle size than that of the first metal oxide particles in a mixed manner.

[0107] Although the content of the metal oxide in the coating solution is suitably controlled depending on a desired porosity of the porous layer and a desired film thickness thereof, it is generally preferable that the content is 5 to 60 mass%.

[0108] In addition, the content can be controlled by calculating a reaction quantity with the phosphate (that is, the produced quantity of a compound containing a metal atom and a phosphorus atom) to be described later so that the surface of the metal oxide is dissolved. It is considered that the produced quantity of the compound containing a metal

atom and a phosphorus atom can be controlled by keeping the surface area of a metal oxide to be used constant.

[0109] That is to say, when porous layers are formed on separate base plates by using metal oxides with different average particle sizes, to keep the produced quantities of compounds each containing a metal atom and a phosphorus atom constant, the surface areas of the metal oxides are kept constant by the following method.

[0110] For example, when a particle A has an average particle radius of r_1, a density of d_1 and a mass of W_1, and when a particle B has an average particle radius of r_2, a density of d_2 and a mass of W_2, the surface area S_1 of the particle A is $3W_1/(r_1 \times d_1)$ and the surface area S_2 of the particle B is $3W_2/(r_2 \times d_2)$. Provided that these surface areas S_1 and S_2 are constant, a used quantity W_2 of the particle B can be determined by the following equation:

$$W_2 = [(r_2 \times d_2)/(r_1 \times d_1)] \times W_1$$

[0111] The phosphate contained in the coating solution used to form the porous layer of the present invention is not particularly limited, and as the phosphate, it is possible to preferably cite, for example, oxo-acids such as phosphinic acid, phosphorous acid, diphosphorous acid, hypophosphoric acid, phosphoric acid (orthophosphoric acid or the like), diphosphoric acid, triphosphoric acid, metaphosphoric acid, peroxophosphoric acid, orthophosphoric acid, polyphosphic acid; salts obtained by substituting a metal atom such as a salt of sodium, a salt of potassium or the like for one to three of hydrogen atoms of these acids; and the like.

[0112] Above all, it is possible to preferably cite phosphoric acids (orthophosphoric acid and the like), salts obtained by substituting a metal atom such as a salt of sodium, a salt of potassium or the like for one to three of hydrogen atoms of these acids, and the like.

[0113] The concentrations or the like of these acids are not particularly limited, and general acids (for example, commercially available ones) can be used.

[0114] Although the content of the phosphate in the coating solution is not particularly limited, the content is preferably 0.05 to 12 mass%, more preferably 0.1 to 10 mass%, and further preferably 0.3 to 8 mass%.

[0115] If the content of the phosphate is less than 0.05 mass%, the layer strength of the porous layer may be low, and if the content exceeds 12 mass%, the porosity of the porous layer may be low.

[0116] As the preferred combination of the metal oxide and the phosphate, for example, when the metal oxide is any of metal oxides such as SiO_2, MgO, ZrO_2, and TiO_2, mixed oxides such as SiO_2/Al_2O_3 and MgO/Al_2O_3, and composite oxides such as $2SiO_2 \cdot 3Al_2O_3$ (mullite), then any of phosphoric acid, sodium dihydrogenphosphate (NaH_2PO_4) and the like is used in combination.

[0117] It is preferable that a dispersant which uniformly disperses a metal oxide, a reaction accelerator which accelerates a reaction of a metal oxide and a compound containing a metal atom and a phosphorus atom, and the like are contained in the coating solution.

[0118] Although the dispersant is not particularly limited, it is possible to use, as the dispersant, citric acid, sodium hexametaphosphate or the like, which are generally known as dispersants for metal oxides or the like. Although the content of the dispersant in the coating solution is not particularly limited, the content is in a range of 0.05 to 1 mass%, preferably in a range of 0.2 to 0.8 mass%, and further preferably in a range of 0.2 to 0.5 mass%.

[0119] Although the reaction accelerator is not particularly limited, it is preferable that any of the following reaction accelerators is used, for example, depending on a metal oxide to be used. In addition, the content of the reaction accelerator (used quantity) is not particularly limited and can be suitably changed depending on a desired film thickness of the porous layer, a desired porosity thereof and the like. A content as described below makes it possible that a compound containing a metal atom and a phosphorus atom is produced at lower temperature, that even if an aluminum plate is used as the base plate, the softening of the aluminum plate is suppressed, and that a lithographic printing plate with excellent characteristics is obtained.

[0120] When SiO_2 is used as the metal oxide, sodium fluoride is preferable, and the content thereof is preferably 1 to 5 mass% with respect to SiO_2.

[0121] When MgO is used as the metal oxide, zirconium phosphate is preferable, and the content thereof is preferably 3 to 30 mass% with respect to MgO.

[0122] When ZrO_2 is used as the metal oxide, aluminum phosphate is preferable, and the content thereof is preferably 3 to 30 mass% with respect to ZrO_2.

[0123] When an oxide containing alumina that is any of mixed oxides such as SiO_2/Al_2O_3 and MgO/Al_2O_3 and composite oxides such as $2SiO_2 \cdot 3Al_2O_3$ (mullite), or TiO_2 is used as the metal oxide, aluminum chloride is preferable, and the content thereof is preferably 5 to 100 mass% with respect to Al_2O_3 or TiO_2, more preferably 10 to 80 mass%.

[0124] It is preferable that the solvent of the coating solution is water.

[0125] The coating solution is prepared by dispersing or dissolving in water a particulate metal oxide and a phosphate, and if required, a dispersant, a reaction accelerator and the like.

[0126] Preferably, a particulate metal oxide is introduced into an aqueous solution containing a dispersant and then dispersed. After it is uniformly dispersed, a phosphate, and a reaction accelerator if required, are introduced into the aqueous solution and then stirred, thus preparing the coating solution.

[0127] The coating solution thus prepared is coated onto the base plate to be described later, and the coating process

is thus completed.

[0128] As a coating method, although various methods can be used, it is possible to cite, for example, bar-coater coating, rotary coating, spray coating, curtain coating, dip coating, air-knife coating, blade coating, roll coating, and the like.

[0129] Next, a drying process is performed, where the coating solution coated on the base plate is heated and dried at 180 to 500°C.

[0130] A drying method is not particularly limited, and a generally used method can be selected. In addition, it is preferable that the drying temperature is 180 to 500°C. If an aluminum plate is used for the base plate, it is preferable that the drying temperature is 180 to 220°C. If the temperature is in this range, the softening of the aluminum plate can be suppressed, and a lithographic printing plate having excellent characteristics can be obtained. In addition, if a metal plate other than an aluminum plate is used for the base plate, since there is no problem of the softening of the metal plate, the drying temperature is not particularly limited but is preferably 180 to 500°C. For example, if a base plate of iron system such as a stainless-steel plate is used, the drying temperature is more preferably 200 to 400°C.

[0131] By performing the drying process, the surface of the particulate metal oxide can be allowed to react with a phosphate, and the particulate metal oxide can be remained without largely reducing the particle size of its own.

[0132] Although the drying time duration is not particularly limited as long as the duration is long enough to remove the water in the coating solution, it is generally preferable that the drying time duration is 10 to 300 seconds, more preferably 30 to 180 seconds.

[0133] Although the porous layer of the present invention can be formed on the base plate by performing the processes described above, another process may be performed besides the processes described above.

[0134] As described above, the porous layer of the present invention can be formed by coating the coating solution containing the particulate metal oxide and phosphate and drying the coating solution. Therefore, the manufacturing process is simple, and the costs can be reduced.

<Sealing Layer>

[0135] The porous layer of the present invention has high porosity and a number of micro pores provided in the surface thereof. Therefore, a presensitized plate may be also manufactured by directly providing an image recording layer on the porous layer provided on the base plate while controlling the porosity into an optimum range. In addition, depending on the porosity, the micro pores may cause a residual color phenomenon in which dye that is a component of an image recording layer enters the micro pores in the porous layer and remains even after development, and a residual layer phenomenon in which, similarly, a binder that is also a component of an image recording layer remains even after development.

[0136] In such a case, sealing treatment for sealing the micro pores in the porous layer of high porosity may be performed before the image recording layer is provided. It is preferable that the sealing treatment is a treatment where a sealing layer (also referred to as "hydrophilic layer" in the present invention) is provided.

[0137] That is to say, it is preferable that the support for a lithographic printing plate of the present invention is a support for a lithographic printing plate provided with a sealing layer on the porous layer of the present invention.

[0138] Although the sealing layer is not particularly limited, preferable is a sealing layer containing a silicate compound and a hydrophilic resin.

[0139] The sealing layer can be prepared by forming a hydrophilic layer comprising a hydrophilic composition on the porous layer of high porosity. Although the film thickness of the sealing layer can be suitably determined depending on a desired hydrophilicity, its characteristics such as strength, and the like, it is generally preferable that the film thickness is in a range of 0.01 to 0.5 μm, more preferably in a range of 0.05 to 0.3 μm. If the film thickness is less than 0.01 μm, a required hydrophilicity may be difficult to be obtained, and if the film thickness exceeds 0.5 μm, the hydrophilic layer may be exfoliated or may be easily cracked by a little curvature at the time of printing or the like.

[0140] In the support for a lithographic printing plate having the porous layer of the present invention and the sealing layer, it is more preferable that the film thickness of the porous layer is 0.5 to 20 μm and the film thickness of the sealing layer is 0.01 to 0.5 μm. The preferred ranges of these film thicknesses are as mentioned above.

[0141] Concerning the measurement of the film thickness of the sealing layer, a fracture face produced by bending a support for a lithographic printing plate provided with the sealing layer is observed with an ultra high-resolution scanning electron microscope (for example, S-900 made by Hitachi, Ltd.). Note that the observation magnification is suitably adjusted depending on the film thickness and the like. Specifically, it is preferable that the magnification is 100 to 10,000 times.

[0142] Moreover, for example, if hollow particles with relatively large sizes such as Silasuballoon are used in the sealing layer, further improvement in performance is possible as well as in the film thickness. In addition, it is possible to form a coating with adiathermancy, hydrophilicity and further strength by using the powder with relatively large sizes and powder particles with small sizes in a mixed manner. This coating can embody a particularly preferable mode of

a support for a lithographic printing plate for a presensitized plate to be provided with a thermosensitive image recording layer.

[0143] Although the optimum coated quantity of the sealing layer varies depending on the film thickness of the porous layer, the quantity and distribution of a photothermal converting agent contained in the image recording layer, the thickness of the image recording layer, the laser scanning rate of an exposure device to be used, the laser output, the exposed beam shape, and the like, the optimum coated quantity can be experimentally determined in a range of 0.01 to 0.5 μm. The coated quantity of the sealing layer and whether or not the porous layer is uniformly sealed can be observed with an electron microscope of high magnification.

[0144] As the silicate compound preferably used in the sealing layer, it is possible to cite water glass of alkali silicates such as sodium silicate, potassium silicate and lithium silicate. Although the content of a silicate compound depends on the kind of a hydrophilic resin to be used together, it is generally preferable that the content is in a range of 30 to 45 mass% as SiO_2 and in a range of 30 to 45 mass% as Na_2O in all the solid contents constituting the sealing layer.

[0145] The silicate compounds, above all, the preferably employed water glass and the like in particular have high hydrophilicity and therefore have a function as a hydrophilizing agent. However, there is a concern that the use of the water glass alone may cause the dehydration and contraction of a coating to generate fine cracking during the drying process and to produce the uneven coating or the like. Accordingly, the use of the water glass alone is poor in layer formation property and therefore may deteriorate the press life. In the present invention, since a hydrophilic resin is used together with the water glass, the hardening behaviors of the water glass and the hydrophilic resin through the drying process are different. Accordingly, a cracking-free uniform coating can be formed by complementary action thereof.

[0146] In addition, a suitable quantity of a hardener for alkali silicates known as the commercial names of CAS, PC-500 and the like (all made by Nissan Chemical Industries, Ltd.), or the like may be added to the silicate compound as an additive.

[0147] In the sealing layer of a support for a lithographic printing plate of the present invention, a preferably employed hydrophilic resin is not particularly limited. As the hydrophilic resin, it is possible to cite various hydrophilic resin compounds and the like, such as publicly known synthetic resins excellent in hydrophilicity including, for example, polyacrylic acid, polyvinyl alcohol, polyvinyl phosphonic acid and the like, and further those known as alkali-soluble resins including novolac resin, phenol-aldehyde resin, m-cresol formaldehyde resin, and p-cresol formaldehyde resin. Note that, if water glass is used as a silicate compound, an acid hydrophilic resin compound is not preferable. This is because, since water glass generally exist as an alkaline sol, if the acid hydrophilic resin compound and water glass are mixed, they gelate, making it difficult to form a uniform coating by a general coating method. In this case, it is preferable that a hydrophilic resin which is soluble in a chemically neutral or alkaline aqueous solvent is used from the viewpoint of manufacturability.

[0148] However, a gel substance obtained by mixing the water glass and acid hydrophilic resin is crushed into fine gel of about 1 μm or less by using a mortar, a high-speed shearing mixer or the like, and the fine gel is fully rinsed with water and dispersed in an alkaline aqueous solvent or water glass again. The gel substance can be used in such a way, in which case, since a predetermined hydrophilicity and coating characteristics can be obtained, the material of the hydrophilic resin is not necessarily limited to a chemically neutral or alkaline hydrophilic resin.

[0149] Although the content of the hydrophilic resin varies depending on a desired hydrophilicity, the characteristics such as layer strength, the kind and quantity of a silicate compound to be used together, it is generally preferable that the content is in a range of 4 to 40 mass% in all the solid contents constituting the sealing layer.

[0150] If a hydrophilic resin is used alone without using the water glass, scum resistance and ink-repelling performance may deteriorate because the hydrophilicity is insufficient.

[0151] It is preferable that the content rate of a silicate compound (SiO_2 + Na_2O (mass%)) to a hydrophilic resin (mass%), that is, ((SiO_2 + Na_2O) (mass%) /hydrophilic resin (mass%)) is in a range of 10 to 99. If the rate of the silicate compound is increased too much, the coating property deteriorates, fine cracking is generated in the coating, and the scum resistance and press life are liable to deteriorate. On the contrary, if the rate of the hydrophilic resin is increased too much, the hydrophilicity deteriorates and scum is likely to be produced in a non-image area.

[0152] Additives such as a plasticizer, a surfactant and a solvent can be used together with the hydrophilic compositions constituting the sealing layer in a range where the effects of the present invention are not damaged, for the purpose of improvement in the handling and film properties of the sealing layer. If a general-purpose polyvinyl alcohol (PVA) or the like is used as the hydrophilic resin in particular, it is preferable to add a suitable quantity of a thermally reactive crosslinking agent such as Elastron BN-69 (made by Dai-Ichi Kogyo Seiyaku Co., Ltd.) in order to improve the water resistance of the sealing layer.

[0153] As a method of forming the sealing layer on the porous layer, it is possible to cite a method in which a hydrophilic composition prepared by mixing the above-described components and an additive to be used as desired is coated onto the porous layer by a spraying method, a bar coating method or the like to form a liquid layer, and the layer is dried with hot air at 100 to 180°C and solidified.

[0154] The porosity of the porous layer thus formed is not particularly limited. Preferably, the porosity of the porous layer is 20% or more and the porosity of the sealing layer is equal to or less than that of the porous layer in the support for a lithographic printing plate having the porous layer of the present invention and the sealing layer. If the porosity of the sealing layer is set to be equal to or less than that of the porous layer, a number of micro pores existent in the surface of the porous layer can be effectively sealed, and the residual color phenomenon and the residual layer phenomenon caused by an image recording layer entering the micro pores can be suppressed. The preferred range of the porosity of the porous layer is as described above.

[0155] Concerning the measurement of the porosity of the sealing layer, a fracture face produced by bending a support for a lithographic printing plate provided with the sealing layer is observed and micrographed with an ultra high-resolution scanning electron microscope (for example, S-900 made by Hitachi, Ltd.). The area percentage of void portions is measured in a range of 3 cm x 3cm of the obtained image data (micrograph). This working is performed at 5 to 10 positions, and the arithmetic average of these measured values is determined as the porosity.

[0156] Note that the observation magnification is suitably adjusted depending on the film thickness of a sealing layer to be observed and the like.

[0157] A more preferable support, as the support for a lithographic printing plate of the present invention, can be obtained by forming the sealing layer on the porous layer. The support exhibits excellent surface hydrophilicity and adiathermancy owing to the characteristics of the porous layer, preferably owing to the characteristics of the porous layer and the sealing layer, and is excellent in the adhesion between the base plate and the porous layer. Moreover, the support has good film properties and is excellent in the adhesion to an image recording layer, other intermediate layers, and the like. Therefore, if a lithographic printing plate is manufactured by using the support, the plate is excellent in sensitivity since the heat generated by exposure is effectively used to form an image, scum is not produced since a non-image area excellent in surface hydrophilicity is excellent in ink-repelling, and the abrasion resistance is improved since the plate is excellent in press life and scratch resistance.

[0158] A presensitized plate can be obtained by providing a thermosensitive image recording layer on the support having the porous layer and the sealing layer. This constitution allows a presensitized plate to be obtained which is excellent in printability and in which formation of a high-sensitivity and high-resolution image is possible where optical energy by exposure, for example, a laser beam used for writing is effectively utilized as thermal energy required to form an image.

<Metal Base Plate>

[0159] The metal base plate for use in the support for a lithographic printing plate of the present invention is not particularly limited. Examples of the metal base plate include a pure aluminum plate, an alloy plate mainly containing aluminum with a trace of a different element, a recycled material of aluminum cans, steel plates other than an aluminum plate, various metal plates each containing a metal element such as Mg, Zr, Si, or Ti as its major component, alloy plates of these elements or metal plates coated with aluminum plating, aluminum foil or the like, a plastic film such as PET on which a metal such as aluminum is laminated or deposited, and the like.

[0160] As the alloy mainly containing aluminum with a trace of a different element, an aluminum alloy plate to be described later is preferably cited. The preferable various metal plates each containing a metal element other than aluminum as its major component, include a stainless-steel plate which is flexible, highly strong and low-priced, a nickel plate, a cupper plate, a magnesium alloy plate, and the like.

[0161] The preferable coated alloy plates or metal plates include the above-mentioned alloy plates and various metal plates each coated with a thin layer of a metal atom, a metal oxide or the like by sputtering, laminating or the like. More preferably, the metal atom or metal oxide is of the same kind as a metal oxide or metal atom in this metal oxide to be used to form the porous layer.

[0162] Above all, as the base plate for use in the present invention, preferable is a plate of the various metal plates free from softening due to heat, which is coated with a thin layer of a metal element or metal oxide of the same kind as a metal oxide or metal atom in this metal oxide to be used to form the porous layer by sputtering, laminating, or the like. In addition, an aluminum plate, which has excellent antirust property and is highly recyclable, easily handled because of its low specific gravity, and low priced, is also preferable.

[0163] The base plate obtained by coating any of the above-mentioned various metal plates, may be obtained by coating the stainless-steel plate, the nickel plate or the like through a sputtering process under usually adopted conditions or through a laminating process and the like.

[0164] Although the thickness of the coating is not particularly limited, it is generally sufficient that the thickness is about 10 nm or more, preferably 10 to 100 nm, and more preferably 25 to 50 nm. In general, if the thickness of the coating is small, any of the various metal plates may be poor in the adhesion to the porous layer of the present invention since the coating cannot sufficiently cover the plate. On the other hand, if the thickness of the coating is large, the price is increased. Therefore, from these points of view, the thickness of the coating is suitably selected in the present

invention.

[0165] For the various metal plates for use in the present invention, the base plates obtained by coating these plates and the like, those commercially available may be used as well.

[0166] Next, description will be given of an aluminum plate which is preferable as the base plate for use in the present invention.

[0167] The composition of the aluminum plate for use in the present invention is not specified. It is possible to suitably use the conventionally and publicly known materials described in Aluminum Handbook, forth edition (published by Japan Light Metal Association (1990)), including, for example, JIS A1050, JIS A1100, JIS A1070, JIS A3004 containing Mn, and Al-Mn system aluminum plates such as International Alloy designation 3103A. In addition, it is also possible to use Al-Mg system alloys and Al-Mn-Mg system alloys (JIS A3005) where 0.1 mass% of magnesium or more is added to these aluminum alloys for the purpose of increasing ultimate tensile strength. Further, it is also possible to use Al-Zr system alloys and Al-Si system alloys containing Zr and Si. Furthermore, Al-Mg-Si system alloys can also be used.

[0168] Regarding the JIS 1050 materials, the technologies proposed by the applicant of the present application are described 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 3-234594 A, JP 1-47545 B, and JP 62-140894 A. In addition, also known are the technologies described in JP 1-35910 B, JP 55-28874 B, and the like.

[0169] Regarding the JIS 1070 materials, the technologies proposed by the applicant of the present application are described 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.

[0170] Regarding the Al-Mg system alloys, the technologies proposed by the applicant of the present application are described in JP 62-5080 B, JP 63-60823 B, JP 3-61753 B, JP 60-203496 A, JP 60-203497 A, JP 3-11635 B, JP 61-274993 A, JP 62-23794 A, JP 63-47347 A, JP 63-47348 A, JP 63-47349 A, JP 64-1293 A, JP 63-135294 A, JP 63-87288 A, JP 4-73392 B, JP 7-100844 B, JP 62-149856 A, JP 4-73394 B, JP 62-181191 A, JP 5-76530 B, JP 63-30294 A, and JP 6-37116 B. In addition, the technologies are also described in JP 2-215599 A, JP 61-201747 A, and the like.

[0171] Regarding the Al-Mn system alloys, the technologies proposed by the applicant of the present application are described in JP 60-230951 A, JP 1-306288 A and JP 2-293189 A. In addition, the technologies are also described in JP 54-42284 B, JP 4-19290 B, JP 4-19291 B, JP 4-19292 B, JP 61-35995 A, JP 64-51992 A, JP 4-226394 A, US 5,009,722, US 5,028,276, and the like.

[0172] Regarding the Al-Mn-Mg system alloys, the technologies proposed by the applicant of the present application are described in JP 62-86143 A and JP 3-222796 A. In addition, the technologies are also described in JP 63-60824 B, JP 60-63346 A, JP 60-63347 A, JP 1-293350 A, EP 223,737 B, US 4,818,300, UK 1,222,777, and the like.

[0173] Regarding the Al-Zr system alloys, the technologies proposed by the applicant of the present application are described in JP 63-15978 B and JP 61-51395 A. In addition, the technologies are also described in JP 63-143234 A, JP 63-143235 A, and the like.

[0174] The Al-Mg-Si system alloys are described in UK 1,421,710 and the like.

[0175] To prepare a plate material from an aluminum alloy, for example, the following method can be adopted. First, a molten aluminum alloy in which the alloy component content is controlled to be a predetermined value is subjected to purification treatment in accordance with a usual method and then to casting. In the purification treatment, in order to remove unnecessary gases such as hydrogen in the molten aluminum alloy, performed is flux treatment; degassing treatment using argon gas, chlorine gas or the like; filtering treatment using a rigid media filter such as a ceramic tube filter or ceramic foam filter, a filter using alumina flakes, alumina balls or the like as filter media, a glass cloth filter or the like; or a combination of the degassing treatment and the filtering treatment.

[0176] It is preferable that these purification treatments are performed to prevent defects caused by non-metal inclusions in the molten aluminum alloy and foreign matters such as oxides, and the defects caused by gases dissolved in the molten aluminum alloy. The filtering of a molten metal is described in JP 6-57432 A, JP 3-162530 A, JP 5-140659 A, JP 4-231425 A, JP 4-276031 A, JP 5-311261 A, JP 6-136466 A, and the like. The degassing of a molten metal is described in JP 5-51659 A and JP 5-49148 U. The applicant of the present application has also proposed a technology concerning the degassing of a molten metal in JP 7-40017 A.

[0177] Next, casting is performed using the molten aluminum alloy subjected to the purification treatment as described above. Concerning a casting method, there are methods: a method, represented by DC casting, in which a solid mold is used; and a method, represented by continuous casting, in which a driven mold is used.

[0178] In the DC casting, the molten aluminum alloy is solidified at a cooling speed in a range of 0.5 to 30°C/sec. If the cooling speed is less than 1°C/sec., a number of coarse intermetallic compounds may be formed. If the DC casting is performed, an ingot with a plate thickness of 300 to 800 mm can be manufactured. Facing is performed on the ingot, if required, in accordance with a usual method, where the outer layer of the ingot is normally cut by 1 to 30 mm, preferably by 1 to 10 mm. Before and after the facing, soaking treatment is performed if required. When the soaking treatment is performed, heating treatment is performed at 450 to 620°C for 1 to 48 hours so as to prevent the interme-

tallic compounds from becoming coarse. If the heating treatment is performed for less than one hour, the effect of the soaking treatment may be insufficient.

[0179] Thereafter, a rolled plate of aluminum is prepared by performing hot rolling and cold rolling. The proper temperatures to start hot rolling are 350 to 500°C. An intermediate annealing treatment may be performed before, after, or in the middle of the hot rolling. The condition of the intermediate annealing treatment is that the plate is heated at 280 to 600°C for 2 to 20 hours, preferably at 350 to 500°C for 2 to 10 hours, by using a batch-type annealing furnace, or that the plate is heated at 400 to 600°C for 6 minutes or less, preferably at 450 to 550°C for 2 minutes or less, by using a continuous annealing furnace. The plate may be heated at a rate of temperature rise of 10 to 200°C/sec. by using a continuous annealing furnace to fine down a crystal structure.

[0180] The flatness of the aluminum plate finished with a predetermined thickness, for example, with a thickness of 0.1 to 0.6 mm by the above-described processes, may be further improved by using a rectification device such as a roller leveler or a tension leveler. Although the improvement of the flatness may be performed after the aluminum plate is cut into sheets, it is preferable that the improvement is performed on the aluminum plate in a continuous coil state in order to increase the productivity. In addition, the plate may be allowed to pass through a slitter line in order to process the plate to have a predetermined plate width. In addition, a thin oil film may be provided on the surface of the aluminum plate in order to prevent the occurrence of scratches caused by mutual frictions of the aluminum plates. A volatile or nonvolatile oil film is suitably used for the oil film depending on requirements.

[0181] On the other hand, as for the continuous casting, a twin-roll casting process (Hunter casting), a process represented by the 3C process in which a cooling roll is used, a twin-belt casting process (Hazelett process), and a process where a cooling belt or cooling block represented by Alusuisse Caster-II type is used, are industrially utilized. If the continuous casting is adopted, the molten aluminum alloy is solidified at a cooling rate in a range of 100 to 1,000°C/sec. The continuous casting has a feature that the solid solution degree of an alloy component to an aluminum matrix can be increased since the cooling rate in the continuous casting is generally higher than that in the DC casting. Regarding the continuous casting, the technologies proposed by the applicant of the present application are described in JP 3-79798 A, JP 5-201166 A, JP 5-156414 A, JP 6-262203 A, JP 6-122949 A, JP 6-210406 A, JP 6-26308 A, and the like.

[0182] In the case of performing continuous casing, for example, if the process, such as the Hunter process, where a cooling roll is used is adopted to perform, a cast plate with a thickness of 1 to 10 mm can be directly and continuously cast, and therefore a merit that a process of hot rolling can be omitted is obtained. In addition, if the process, such as the Hazelett process, where a cooling belt is used is adopted to perform, a cast plate with a thickness of 10 to 50 mm can be cast, and a continuous casting rolled plate with a thickness of 1 to 10 mm can be obtained generally by disposing a hot reduction roll immediately after the casting and continuously rolling the plate.

[0183] These continuous casting rolled plates are each finished into a plate with a predetermined thickness, for example, with a thickness of 0.1 to 0.6 mm though the processes such as cold rolling, intermediate annealing, improving of flatness, and slitting, similarly to the case as described in the DC casting. Regarding intermediate annealing conditions and cold rolling conditions in the case of using the continuous casting, the technologies proposed by the applicant of the present application is described in JP 6-220593 A, JP 6-210308 A, JP 7-54111 A, JP 8-92709 A, and the like.

[0184] The aluminum plate thus manufactured is desired to have various characteristics as described below.

[0185] As for the strength of an aluminum plate, it is preferable that the 0.2 % proof stress is 140Mpa or more in order to obtain a required elastic strength as a support for a lithographic printing plate. In addition, in order to obtain an elastic strength of a certain degree even when burning treatment is performed, it is preferable that the 0.2 % proof stress after heat treatment at 270°C for 3 to 10 minutes is 80Mpa or more, more preferably 100MPa or more. If the aluminum plate is desired to have elastic strength in particular, it is possible to adopt an aluminum material to which Mg or Mn is added. However, if the elastic strength is increased, the fittability to a plate cylinder of a printing machine is deteriorated. Therefore, the material and the added quantity of a trace component are suitably selected depending on the applications of the aluminum plate. In this regard, the technologies proposed by the applicant of the present application is described in JP 7-126820 A, JP 62-140894 A, and the like.

[0186] It is preferable the crystal structure of the aluminum plate is not so coarse on the surface of the aluminum plate because, if chemical or electrochemical graining treatment is performed, the crystal structure on the surface of the aluminum plate may cause defective surface quality. The crystal structure on the surface of the aluminum plate is preferably 200 μm or less in width, more preferably 100 μm or less, further preferably 50 μm or less. In addition, the crystal structure is preferably 5,000 μm or less in length, more preferably 1,000 μm or less, further preferably 500 μm or less. In this regard, the technologies proposed by the applicant of the present application are described in JP 6-218495 A, JP 7-39906 A, JP 7-124609 A, and the like.

[0187] It is preferable that the alloy component distribution on the surface of the aluminum plate is not very uneven because, if chemical or electrochemical graining treatment is performed, the uneven distribution of the alloy components on the surface of the aluminum plate may cause defective surface quality. In this regard, the technologies proposed by the applicant of the present application is described in JP 6-48058 A, JP 5-301478 A, JP 7-132689 A, and

the like.

[0188] As for the intermetallic compounds in the aluminum plate, the size and density of an intermetallic compound may affect the chemical graining treatment and electrochemical graining treatment. In this regard, the technologies proposed by the applicant of the present application are described in JP 7-138687 A, JP 4-254545 A, and the like.

[0189] In the present invention, the aluminum plate as shown above may be provided, in the final rolling process, with irregularities by pack rolling, transfer or the like to use.

[0190] The aluminum plate to be used in the present invention is a continuous belt-like sheet material or a plate material. That is, the material may be an aluminum web or may be a sheet cut into a size corresponding to a presensitized plate to be shipped as a product, or the like.

[0191] Since there is a possibility that a scratch on the surface of the aluminum plate may become a defect when the aluminum plate is processed into a support for a lithographic printing plate, it is necessary to suppress the occurrence of scratches as little as possible in a step before the surface treatment process where the support for a lithographic printing plate is manufactured. For this, it is preferable that the aluminum plate is packed in a stable form, with a packing style which hardly causes any scratch on the aluminum plate during transportation.

[0192] In the case of the aluminum web, as a packing style for the aluminum, for example, a hard board and a piece of felt are laid on an iron pallet; corrugated doughnut boards are attached to both ends of the product; the entire product is wrapped with a poly tube; a wooden doughnut is inserted into the inner diameter section of the coil; a piece of felt is attached to the outer periphery of the coil; the packing is tightened by a hoop iron; and an indication is applied onto the outer periphery. In addition, it is possible to use a polyethylene film as the packing material and to use needle felt and a hard board as the buffer material. Although there are various packing modes other than those described above, the packing method is not limited to this as long as the transportation and the like of the product can be done in a stable manner and without causing any scratch thereon.

[0193] Although the plate thickness of the base plate for use in the present invention is not particularly limited, the plate thickness is preferably about 0.1 to 0.6 mm, more preferably 0.15 to 0.4 mm, and further preferably 0.2 to 0.3 mm.

<Surface Treatment>

[0194] By providing the porous layer on the metal base plate on which the pretreatment has been performed according to the present invention, both scum resistance and press life can be achieved when a lithographic printing plate is manufactured, and the lithographic printing plate excellent in the adhesion between the porous layer and the base plate and excellent in printing performance can be obtained. However, the surface treatment of a base plate which is generally performed in manufacturing of a lithographic printing plate (for example, publicly known various graining treatments and the like) can be also performed.

[0195] The support for a lithographic printing plate of the present invention can be manufactured through simple processes such as coating of a coating solution and drying even without performing surface treatment, and is excellent in sensitivity, scum resistance and press life. Therefore, the manufacturing costs can be reduced in comparison with those of a conventional support for a lithographic printing plate which is subjected to graining treatment to prepare.

[Presensitized Plate]

[0196] The presensitized plate of the present invention can be manufactured by providing an image recording layer such as a photosensitive layer, thermosensitive layer or the like as exemplified below on the foregoing support for a lithographic printing plate of the present invention.

<Image Recording Layer>

[0197] In the image recording layer for use in the present invention, a photosensitive composition is used.

[0198] Examples of the photosensitive composition preferably used in the present invention include: a thermal positive type photosensitive composition containing an alkali-soluble high-molecular compound and a photothermal converting substance (hereinafter, this composition and an image recording layer using this composition are referred to as "thermal positive type"); a thermal negative type photosensitive composition containing a curing compound and a photothermal converting substance (hereinafter, similarly referred to as "thermal negative type"); and a photosensitive composition dispensing with a specific development process (hereinafter, similarly referred to as "development dispensable type"). Hereinafter, description will be given of these preferable photosensitive compositions.

<Thermal Positive Type>

<Photosensitive Layer>

[0199] The thermal positive type photosensitive composition contains a water-insoluble and alkali-soluble high-molecular compound (referred to as "alkali-soluble high-molecular compound" in the present invention) and a photothermal converting substance. In the thermal positive type image recording layer, the photothermal converting substance converts light energy such as an infrared laser beam into heat, and the heat efficiently releases an interaction which deteriorates the alkali solubility of the alkali-soluble high-molecular compound.

[0200] The alkali-soluble high-molecular compounds include, for example, a resin containing an acid group in a molecule thereof and a mixture of two kinds or more of the resin. A resin having an acid group such as a phenolic hydroxy group, sulfonamide group ($-SO_2NH-R$ (where, R is a hydrocarbon group.)), or active imino group ($-SO_2NHCOR$, $-SO_2NHSO_2R$, $-CONHSO_2R$ (where, R is the same as above.)), is particularly preferable in terms of the solubility to an alkaline developer.

[0201] Above all, a resin having a phenolic hydroxy group is preferable because the resin is excellent in image formation performance in exposure by the light of an infrared laser or the like. The preferable resins include, for example, novolac resins such as phenol formaldehyde resin, m-cresol-formaldehyde resin, p-cresol-formaldehyde resin, m-/p-mixed cresol-formaldehyde resin, and phenol/cresol (may be any one of m-, p- and m-/p- mixed one) mixed-formaldehyde resin (phenol-cresol-formaldehyde co-condensed resin).

[0202] Further, the preferable compounds also include the high-molecular compounds described in JP 2001-305722 A (particularly, [0023] to [0042]), the high-molecular compounds containing a repeated unit represented by the general formula (I) described in JP 2001-215693 A, and the high-molecular compounds described in JP 2000-311570 A (particularly [0107]).

[0203] The preferable photothermal converting substances include pigments or dyes which have a light absorbing area in the infrared area where the wavelength is 700 to 1,200 nm in terms of the sensitivity in recording. The dyes include, for example, azo dye, metal complex azo dye, pyrazolone azo dye, naphthoquinone dye, anthraquinone dye, phthalocyanine dye, carbonium dye, quinone imine dye, methine dye, cyanine dye, squarylium dye, a pyrylium salt, a metal thiolate complex (for example, nickel thiolate complex). The cyanine dye is preferable above all, and the cyanine dye represented by the general formula (I) described in JP 2001-305722 A is particularly preferable.

[0204] A solubility inhibitor can be contained in the thermal positive type photosensitive composition. Preferable solubility inhibitors include, for example, the solubility inhibitor as described in JP 2001-305722 A, [0053] to [0055].

[0205] In addition, it is preferable to allow the thermal positive type photosensitive composition to contain, as additives, a sensitivity controlling agent, a printing-out agent for obtaining a visible image immediately after a plate is heated by exposure, compounds such as dyes as image coloring agents, and a surfactant for improving coating property and treatment stability. For these compounds, the compounds as described in JP 2001-305722 A, [0056] to [0060] are preferable.

[0206] The photosensitive composition described in detail in JP 2001-305722 A is preferably used, even though it is preferable from other viewpoints than the above.

[0207] In addition, the thermal positive type image recording layer is not limited to a single layer and may have a double layer structure.

[0208] Preferable image recording layers of a double layer structure (multilayer type image recording layer) includes a type where a lower layer (hereinafter, referred to as "A layer") excellent in press life and solvent resistance is provided on a side closer to a support and a layer (hereinafter, referred to as "B layer") excellent in a positive image formation property is provided thereon. This type is of high sensitivity and can realize broad development latitudes. The B layer generally contains a photothermal converting substance. Preferable photothermal converting substances include the aforementioned dyes.

[0209] Preferable resins to be used for the A layer include polymers which have, as copolymerized components, monomers having a sulfonamide group, an active imino group, a phenolic hydroxy group, or the like because the polymers are excellent in press life and solvent resistance. Preferable resins to be used for the B layer include an alkaline aqueous solution soluble resin having a phenolic hydroxy group.

[0210] In addition to the above-mentioned resins, various additives can be contained in the compositions used for the A layer and B layer if required. Specifically, the various additives as described in JP 2002-3233769 A, [0062] to [0085] are preferably used. Moreover, the additives described in the above-mentioned JP 2001-305722 A, [0053] to [0060] are also preferably used.

[0211] It is preferable that respective components constituting the A layer and B layer and the contents thereof are adjusted as described in JP 11-218914 A.

<Intermediate Layer>

[0212] It is preferable to provide an intermediate layer between the thermal positive type image recording layer and the support. Preferable components to be contained in the intermediate layer include the various organic compounds described JP 2001-305722 A, [0068].

<Others>

[0213] For a method of manufacturing the thermal positive type image recording layer and a plate making method, the method described in detail in JP 2001-305722 A can be used.

<Thermal Negative Type>

[0214] The thermal negative type photosensitive composition contains a curing compound and a photothermal converting substance. The thermal negative type image recording layer is a negative type photosensitive layer where a portion irradiated by the light of an infrared laser or the like is cured to form an image portion.

<Polymerization Layer>

[0215] As one of the thermal positive type image recording layers, a polymerization type image recording layer (a polymerization layer) can be preferably cited. The polymerization layer contains a photothermal converting substance, a radical initiator, a radically polymerizing compound which is a curing compound, and a binder polymer. In the polymerization layer, the photothermal converting substance converts an absorbed infrared ray into heat; the heat causes the radical initiator to be decomposed to generate a radical; the generated radical initiates a chain reaction of polymerization of the radically polymerizing compound; and thus the polymerization layer is cured.

[0216] The photothermal converting substances include, for example, the photothermal converting substances used for the above-described thermal positive type. Concrete examples of the particularly preferable cyanine dye include those described in JP 2001-133969 A, [0017] to [0019].

[0217] The preferable radical initiators include an onium compound. The onium compounds described in JP 2001-133969 A, [0030] to [0033] are particularly preferable.

[0218] The radically polymerizing compounds include a compound having at least one, preferably 2 or more, of terminal ethylenic unsaturated bonds.

[0219] The binder polymers include a linear organic polymer. The preferable ones include a linear organic polymer which is soluble or swells in water or a weak alkaline water solution. Above all, an (metha)acrylic resin having a benzyl group or an unsaturated group such as an allyl group or acryloyl group, and a carboxyl group as side chains, is preferable because the resin has excellent balance of the film strength, sensitivity and development performance.

[0220] For the radically polymerizing compound and binder polymer, those described in detail in JP 2001-133969 A, [0036] to [0060] can be used.

[0221] It is preferable to allow the thermal negative type photosensitive composition to contain the additives described in JP 2001-133969 A, [0061] to [0068] (for example, a surfactant for improving the coating property).

[0222] For a method of manufacturing the polymerization layer and a plate making method, the methods described in detail in JP 2001-133969 A can be used.

<Acid Crosslinking Layer>

[0223] In addition, as one of the thermal negative type image recording layers, an acid crosslinking type image recording layer (acid crosslinking layer) can be preferably cited. The acid crosslinking layer contains a photothermal converting substance, a thermal acid initiator, a compound (crosslinking agent) which is crosslinked by an acid that is a curing compound, and an alkali-soluble high-molecular compound which is capable of reacting with the crosslinking agent in the presence of an acid. In the acid crosslinking layer, the photothermal converting substance converts an absorbed infrared ray into heat; the heat causes the thermal acid initiator to be decomposed to generate an acid; the generated acid reacts the crosslinking agent with the alkali-soluble high-molecular compound; and thus the acid crosslining layer is cured.

[0224] The photothermal converting substances include the same ones as used in the polymerized layer. The thermal acid initiators include, for example, thermally decomposing compounds such as a photoinitiator for photopolymerization, color changing agents of dyes, and an acid initiator used for micro resist, and the like.

[0225] The crosslinking agents include, for example, aromatic compounds substituted by a hydroxymethyl group or alkoxymethyl group; compounds having an N-hydroxymethyl group, N-alkoxymethyl group or N-acyloxymethyl group;

and epoxy compounds.

[0226] The alkali-soluble high-molecular compounds include, for example, novolac resin and a polymer having a hydroxyaryl group as a side chain.

<Non-treated Type>

[0227] The non-treated type photosensitive compositions include those of a thermoplastic particulate polymer type, a micro-capsule type, a sulfonic acid initiating polymer-contained type and the like. Each of these compounds is of a thermosensitive type containing a photothermal converting substance. It is preferable that the photothermal converting substance is the same dye as used in the aforedescribed thermal positive type.

[0228] The thermoplastic particulate polymer type photosensitive composition is one in which a hydrophobic and a hot-melt particulate polymer is dispersed in a hydrophilic high-molecular matrix. In the thermoplastic particulate polymer type image recording layer, the hydrophobic particulate polymer is melted by heat generated by light exposure, and the melted polymers are mutually welded to form a hydrophobic area, that is, an image area.

[0229] For the particulate polymer, a particulate polymer in which the particulates are melted to mutually coalesce by heat is preferable, and a particulate polymer which has a hydrophilic surface and can be dispersed in a hydrophilic component such as dampening water is more preferable. Specifically, the preferable thermoplastic particulate polymers include those described in "Research Disclosure" No. 33303 (January in 1992), JP 9-123387 A, JP 9-131850 A, JP 9-171249 A, JP 9-171250 A, EP 931,647 A, and the like. Above all, polystyrene and poly(methyl methacrylate) are preferable. The particulate polymers having a hydrophilic surface include a polymer which is hydrophilic itself; and a particulate polymer whose surface is made hydrophilic by allowing the surface to adsorb a hydrophilic compound such as polyvinyl alcohol or polyethylene glycol.

[0230] It is preferable that the particulate polymer has a reactive functional group.

[0231] The preferable micro-capsule type photosensitive compositions include those described in JP 2000-118160 A and those of a micro capsule type which contains a compound having a thermally reactive functional group as described in JP 2001-277740 A.

[0232] The sulfonic acid initiating polymers used for the sulfonic initiating polymer-contained type photosensitive composition include, for example, polymers having a sulfonate group, a disulfonate group, or a sec- or tert-sulfonamide group as a side chain, descried in JP 10-282672 A.

[0233] By allowing the non-treated type photosensitive composition to contain a hydrophilic resin, not only the developing property on a printing machine becomes better but also the film strength of the photosensitive layer itself is improved. The preferable hydrophilic resins include, for example, a resin having a hydrophilic group such as a hydroxy group, a carboxyl group, a hydroxyethyl group, a hydroxypropyl group, an amino group, an aminoethyl group, an aminopropyl group, or a carboxymethyl group; and a hydrophilic sol-gel conversion system binding resin.

[0234] The non-treated type image recording layer can be developed on a printing machine, dispensing with a specific development process. For a method of manufacturing the non-treated type image recording layer and a method of plate making and printing, methods described in detail in JP 2002-178655 A.

<Overcoat Layer>

[0235] In the presensitized plate of the present invention, it is possible to provide a water-soluble overcoat layer on the above-described image recording layer in order to prevent the surface of a thermosensitive layer from being polluted by an oleophilic substance. It is preferable that the water-soluble overcoat layer used in the present invention can be easily removed at the time of printing. The overcoat layer contains a resin selected from water-soluble organic high-molecular compounds.

[0236] As for the water-soluble organic high-molecular compounds, a layer containing the compound, formed by coating and drying, has a film formation capacity. More specifically, the water-soluble organic high-molecular compounds include, for example, polyvinyl acetate (however, those with a hydrolysis ratio of 65% or higher), polyacrylic acid and its alkali metal compounds or amine compounds, polyacrylic acid copolymer and its alkali metal compounds or amine compounds, polymethacrylic acid and its alkali metal compounds or amine compounds, polymethacrylic acid copolymer and its alkali metal compounds or amine compounds, polyacrylamide and its copolymer, polyhydroxyethylacrylate, polyvinylpyrrolidone and its copolymer, polyvinylmethyl ether, polyvinylmethyl ether/maleic anhydride copolymer, poly-2-acrylamido-2-methyl-1-propanesulfonic acid and its alkali metal compounds or amine compounds, poly-2-acrylamido-2-methyl-1-propanesulfonic acid copolymer and its alkali metal compounds or amine compounds, gum arabic, cellulose derivatives (for example, carboxymethylcellulose, carboxyethylcellulose, methylcellulose and the like) and their denatured resins, white dextrin, pullulan, enzymolysis etherified dextrin, and the like. In addition, a mixture of two kinds or more of these resins can be also used depending on the application thereof.

[0237] In addition, a water-soluble photothermal converting agent of the afore-mentioned photothermal converting

agents may be added to the overcoat layer. Further, in order to secure the evenness of coating, if an aqueous solution is used for coating, non-ionic surfactants such as poly(oxyethylene)nonylphenyl ether or poly(oxyethylene)dodecyl ether can be added to the overcoat layer.

[0238] The dried coated quantity of the overcoat layer is preferably 0.1 to 2.0 g/m^2. Within this range, the surface of the thermosensitive layer can be well prevented from being fouled with an oleophilic substance such as a fingerprint stain without damaging the development property on a printing machine.

<Back Coating>

[0239] A coating layer comprising an organic high-molecular compound can be provided, if required, on the back face of the presensitized plate of the present invention, which is thus obtained by providing any of the various image recording layers on the support for a lithographic printing plate of the present invention, in order to prevent the image recording layers from being scratched when they are stacked.

<Method of Manufacturing Presensitized Plate>

[0240] Each layer such as an image recording layer can be generally manufactured by coating a coating solution obtained by solving the above-mentioned components in a solvent, onto a support for a lithographic printing plate.

[0241] The solvents to be used here include ethylene dichloride, cyclohexane, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethyl urea, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, γ-butyrolactone, toluene, water, and the like. However, the solvents according to the present invention are not limited to these. These solvents are used alone or in mixture.

[0242] The concentration of the afore-mentioned components (all solid components) in the solvent are preferably 1 to 50 mass%.

[0243] As a coating method thereof, various methods can be used, including, for example, bar coater coating, rotary coating, spray coating, curtain coating, dip coating, air-knife coating, blade coating, roll coating, and the like.

[Plate Making (Method of Manufacturing Presensitized Plate)]

[0244] The lithographic printing plate is manufactured from the presensitized plate using the support for a lithographic printing plate of the present invention by various methods according to the image recording layers.

[0245] Light sources of an active light beam used for image exposure include, for example, a mercury lamp, a metal halide lamp, a xenon lamp, a chemical lamp. Laser beams include, for example, beams of helium-neon laser (He-Ne laser), argon laser, krypton laser, helium-cadmium laser, KrF excimer laser, semiconductor laser, YAG laser, YAG-SGH laser.

[0246] After exposure using the above-mentioned light source and laser, if the image recording layer is of a thermal positive or thermal negative type, it is preferable that a lithographic printing plate is obtained by performing development using a developer after the exposure.

[0247] It is preferable that the developer is an alkaline developer, more preferably an alkaline aqueous solution containing substantially no organic solvent.

[0248] In addition, a developer containing substantially no alkali metal silicate and containing a saccharide (a developer containing substantially no alkali metal silicate) is also preferable. For a method of performing development using the developer containing substantially no alkali metal silicate, it is possible to use the method described in detail in JP 1-109637 A.

[0249] In addition, a developer containing an alkali metal silicate can be also used.

[0250] If the treatment method of a presensitized plate, where development is performed using the developer containing substantially no alkali metal silicate, is used, it is possible to prevent the occurrence of problems which arise when development is performed by using a developer containing an alkali metal silicate, specifically, a problem that a solid attributable to SiO_2 is likely to deposit, a problem that gel attributable to SiO_2 is produced in neutral treatment where the wastewater of a developer is treated, and the like.

[0251] The presensitized plate of the present invention is a presensitized plate prepared by providing the image recording layer on the support for a lithographic printing plate which has been prepared by providing, on a metal base plate after subjected to a specific pretreatment, a porous layer that has high film strength and is excellent in scratch resistance and adiathermancy. Therefore, the presensitized plate of the present invention is excellent in sensitivity, also excellent in scum resistance and press life when processed into a lithographic printing plate, and further, excellent in adhesion between the metal base plate and the porous layer.

Examples

[0252] Hereinafter, the present invention will be described more concretely by showing examples. However, the present invention is not limited to these examples.

[Examples 1 to 22]

<Preparation of Porous Layer Coating Solution>

[0253] Coating solutions C-1 to C-8 of the compositions shown in Table 1 were each prepared by the following methods.

[0254] Specifically, 0.1 g of citric acid was introduced into a suitable quantity of water as a dispersant. After it was stirred for some period of time, a metal oxide shown in Table 1 was added thereto in accordance with a quantity (g) to be used shown in Table 1 and the metal oxide was evenly dispersed for about 10 minutes using an ultrasonic dispersing device (Ultrasonic Homogenizer, VC-130, made by Sonis & Materials, Inc.) and a homogenizer (Auto Cell Master, CM-200, made by AS ONE Corporation).

[0255] Thereafter, a phosphate and a reaction accelerator shown in Table 1 were added to the resultant water in accordance with respective quantities to be used shown in Table 1, and the mass of the obtained entire coating solution was adjusted to 100g by further adding water thereto. Thus, each of the coating solutions C-1 to C-8 was obtained. For reference, Table 1 shows, as the film thickness (μm), film thicknesses and porosities after the respective coating solutions were coated on identical bars without being undiluted and then dried.

[0256] For the metal oxides shown in Table 1, those commercially available were used as they were or after the average particle sizes thereof were controlled by crushing.

[0257] Specifically, for "Al_2O_3" to be used for the coating solution C-1, used was AKP-50 (average particle size: 0.3 μm, made by Sumitomo Chemical Co., Ltd.).

[0258] For "MgO" to be used for the coating solution C-2, used was Ube Materials 2000A (average particle size: 0.2 μm, made by Ube Industries, Ltd.).

[0259] For "ZrO_2" to be for the coating solution C-3, used was Spherical Silica Containing Zirconia (commercial name) (average particle size: 0.7 μm, made by Admatechs Co., Ltd.).

[0260] For "SiO_2" to be used for the coating solution C-4, used was SO-C1 (commercial name) (particle size: 0.2 to 0.3 μm (average particle size: 0.25 μm), made by Admatechs Co., Ltd.).

[0261] For "SiO_2/Al_2O_3" to be used for the coating solution C-5, used was Nano Tek series (generally called ultrafine particles) SiO_2/Al_2O_3 (a mixed oxide with an average particle size of 0.03 μm, made by C.I. Kasei Co., Ltd.).

[0262] For "MgO/Al_2O_3" to be used for the coating solution C-6, used was Nano Tek series (generally called ultrafine particles) MgO/Al_2O_3 (a mixed oxide with an average particle size of 0.05 μm, made by C.I. Kasei Co., Ltd.).

[0263] For "Mullite (powder)" to be for the coating solution C-7, used was Alumina-Silica Composite Oxide (commercial name) (average particle size: 0.6 μm, made by Admatechs Co., Ltd.).

[0264] For "TiO_2" to be used for the coating solution C-8, used was a reagent (amorphous, average particle size: 0.05 μm, made by Wako Pure Chemical Industries, Ltd.).

[0265] For the phosphoric acid, citric acid, sodium fluoride, zirconium phosphate and aluminum chloride, used were reagents thereof made by Kanto Kagaku.

[0266] As for the crushed materials, the average particle sizes were controlled by changing crushing time duration from 1 to 100 hours at a revolution of about 100 rpm using a mill such as HD A-5 pot mill (YTZ-0.2, Nikkato Corporation).

[0267] Note that the quantity of the metal oxide to be used for each coating solution was calculated and controlled by the following equation so that the reaction quantity thereof with a phosphate (that is, a produced quantity of a compound containing a metal atom and a phosphorus atom) would be constant.

[0268] When the average particle radius, density and mass of MgO particles for the coating solution C-2 were r_1, d_1 and W_1 respectively, and when the average particle radius, density and mass of metal oxide particles for each coating solution other than the coating solution C-2 were r_2, d_2 and W_2 respectively, then the quantity of the metal oxide particles to be used for each coating solution other than the coating solution C-2 was calculated from the following equation. Note that the actual added quantity of the particles (the quantity of a metal oxide to be used in Table 1) was determined based on the calculated value from the following exemplified equation, considering the actual coated image quality, the film strength and the like.

$$W_2 = [(r_2 \times d_2) / (r_1 \times d_1)] \times W_1$$

Table 1

Coating solution	Metal oxide		Phosphate		Dispersant	Reaction accelerator		Drying temperature of coating solution	Thickness of film	Porosity
	Kind	Quantity of used material (g)	Kind	Quantity of used material (g)	(g)	Kind	Quantity of used material (g)	(°C)	(μm)	(%)
C-1	Al_2O_3	44	H_3PO_4	5.5	0.1	$AlCl_3$	4	180	5.5	50
C-2	MgO	26	H_3PO_4	5.5	0.1	Aluminum phosphate	4	220	3.2	40
C-3	ZrO_2	100	H_3PO_4	5.5	0.1	Aluminum phosphate	4	300	18	30
C-4	SiO_2	26	H_3PO_4	5.5	0.1	NaF	1	260	3.3	50
C-5	Complex of SiO_2/ Al_2O_3	3.7	H_3PO_4	5.5	0.1	$AlCl_3$	1	270	0.5	30
C-6	Complex of MgO/ Al_2O_3	7.3	H_3PO_4	5.5	0.1	$AlCl_3$	1	220	0.9	30
C-7	Mullite	73	H_3PO_4	5.5	0.1	$AlCl_3$	4	240	9	50
C-8	TiO_2	7.3	H_3PO_4	5.5	0.1	$AlCl_3$	1	240	0.9	30

<Preparation of Plate>

[0269] The plates are prepared by performing any of undermentioned pretreatments in accordance with parameters as shown in Table 2 using various base plates shown below, each with a thickness of 0.24 mm or less.

Metal base plate 1: aluminum plate (JIS 1050 material (made by Sumitomo Light Metal Industries, Ltd.))
Metal base plate 2: aluminum plate (JIS 3005 material (made by Sumitomo Light Metal Industries, Ltd.))
Metal base plate 3: recycled material of aluminum cans (with an Al purity of 87 mass%)
Metal base plate 4: aluminum-plated steel plate (Alster steel plate (made by Nisshin Steel Co., Ltd.), quantity of aluminum plating: 120g/m^2, 67 μm (on both sides), MSA-T-BM-120)
Metal base plate 5: aluminum foil-laminated polyethylene terephthalate resin (commercial name: Alpet 1025 (made by Kosumo Kasei Kogyo KK, laminated quantity: 10 μm)
Metal base plate 6: magnesium plate (Mg purity 99.99% material (made by Nilaco Corporation))
Metal base plate 7: zirconium plate (Zr material, purity: 99.7%, (made by Nilaco Corporation))
Metal base plate 8: silicone plate (Si wafer material, purity: 99.999%, (made by Nilaco Corporation))
Metal base plate 9: titanium plate (Ti material, purity: 99.5 %, (made by Nilaco Corporation))

1) Acid treatment 1: Dipping treatment was performed on a metal base plate in an aqueous solution of sulfuric acid with a concentration of 360g/L. The treatment conditions were a temperature of 60°C and a time period of 60 seconds. Thereafter, the plate was rinsed with water and dried.
2) Alkali-acid treatment: Dipping treatment was performed on a metal base plate in an aqueous solution of sodium hydroxide with a concentration of 360g/L at 70°C for 10 seconds. Thereafter, the plate was rinsed with water and dried, and then dipping treatment was performed on the plate in an aqueous solution of sulfuric acid with a concentration of 360g/L at 60°C for 60 seconds.
3) Anodizing treatment: The treatment was performed on a metal base plate in an aqueous solution of sulfuric acid with an electrolytic solution concentration of 170g/L under the following conditions: a solution temperature of 33°C; a current density of 5A/dm^2; a voltage of 15V; and an electrolysis time period of 10 seconds (constant current). In this case, the thickness of the anodic oxide coating was about 0.1 μm.

<Preparation of Support for Lithographic Printing Plate>

[0270] Based on the combinations of the plates and coating solutions shown in Table 2, each coating solution was applied onto the corresponding plate so that the thickness of the dried coating became the thickness shown in Table 2 by diluting the mother liquor of each coating solution shown in Table 1 with water and further by controlling the count of a commercial wire bar. The coated plates were dried at the respective drying temperatures shown in Table 1, thus forming porous layers.

[0271] Note that the thickness of the porous layer was adjusted by changing the size of wire of the commercial wire bar from No. 1.6 (coated quantity: about 3 cc/m^2) to No. 28 (coated quantity: about 53 cc/m^2) to select a wire size with which a desired thickness was obtained.

[0272] In addition, although the drying time period depends on the film thickness (μm) of the porous layer, as a guide, a time period calculated by 30 seconds + 20 seconds × (film thickness - 1) was adopted as the drying time period. Specifically, when the film thickness was 5.5 μm, the time period was 30 + 20 × (5.5 - 1) = 120 seconds.

[0273] If a sealing layer was coated, a sealing layer coating solution having the following composition was applied on the porous layer formed as described above, using a commercial wire bar so that the thickness of the dried coating became the film thickness shown in Table 2. The applied coating was then dried at 120°C for 2 minutes to form the sealing layer, and thus the support for a lithographic printing plate of the present invention was obtained.

(Composition of Sealing Layer Coating Solution)

[0274]

- No. 3 sodium silicate (reagent, made by Kanto Kagaku) as a silicate: 10 g
- AIMATEX E269 (emulsion resin, made by Mitsui Chemicals, Inc.) as a hydrophilic resin: 0.4 g
- Water: 50 g

[Comparative Examples 1 to 3]

<Preparation of Support for Lithographic Printing Plate>

[0275] The pretreatment according to the present invention was not performed on the aluminum plate of Metal base plate 1 used in Examples described above, and the coating solution C-1 used in Examples was applied on this aluminum plate and dried similarly to Examples, thus forming a porous layer with the film thickness shown in Table 2.

[0276] Incidentally, in Table 2, when the treatment of each title was not performed, the corresponding fields are indicted by "-."

2. Evaluation of Porous Layer and Sealing Layer

<Porosity of Porous Layer>

[0277] For the measurement of the porosity of the porous layer, the porosity was determined from the film thickness of the porous layer shown in Table 2 and the mass of the porous layer after dried. The results are shown in Table 1.

[0278] More specifically, the density of the porous layer was calculated by the following equation from the film thickness of the porous layer and the film mass per unit area thereof:

$$\text{Density } (g/cm^3) = (\text{Film mass per unit area}/\text{Film thickness}).$$

[0279] The porosity was calculated by the following equation using the calculated density:

$$\text{Porosity } (\%) = \{1 - (\text{Density of Porous Layer}/D)\} \times 100$$

where D is a density (g/cm^3) according to the Handbook of Chemistry, of any of the metal oxides used to form the porous layer.

[0280] Note that the film mass per unit area of the porous layer was measured by a generally-called Mason method. The film thicknesses of the porous layers shown in Table 2 are values measured by observing the porous layers at the following magnifications depending on the film thicknesses with an ultra-high resolution scanning electron microscope.

[0281] The magnification was set to 10,000 times when the film thickness was 1 μm or less, the magnification was set to 3,000 times when was 1 to 5 μm, and the magnification was set to 100 to 3,000 times when the film thickness was 5 μm or more.

<Porosity of Sealing Layer>

[0282] In measurement of the film thickness of the porous layer, a fracture face produced by bending each of the supports for lithographic printing plates obtained in Examples described above, is observed and micrographed at a magnification of 50,000 times with an ultra-high resolution scanning electron microscope (S-900, made by Hitachi, Ltd.). Since any void part was not observed in any of the supports for lithographic printing plates, in a range of 3 cm × 3 cm of the obtained image data (micrographs), the porosity was determined to be "0%," which is shown in Table 2.

<Adhesion>

[0283] The adhesion of the porous layer to each of the supports for lithographic printing plates obtained in Examples 1 to 22 and Comparative Examples 1 to 3, was evaluated by the following methods. The results are shown in Table 2.

[0284] For an adhesion evaluation method, a test was performed by weighting each porous layer with 1.5 kg using a continuously weighting-type scratch strength tester SB62 TYPE18 (made by Shinto Kagaku KK.) under the following conditions: a sapphire needle with a diameter of 0.4 mm; and a needle moving speed of 1m/min. For the evaluation, the abraded part was visually observed and the state of an abrasion trace was evaluated.

[0285] As the results, a case where no change was observed is indicated by "A," a case where a slight abrasion trace was observed on the surface is indicated by "B," a case where an apparent abrasion trace was observed is indicated by "C," and a case where the surface of the base plate was exposed is indicated by "D."

<Interfacial Exfoliation Resistance>

[0286] For evaluation of the interfacial exfoliation resistance of the porous layer of each of the supports for lithographic printing plates obtained in Examples 1 to 22 and Comparative Examples 1 to 3, the obtained support sample was bent, and the bent part was observed with an ultra high-resolution scanning electron microscope (S-900, made by Hitachi, Ltd.). The exfoliated state of the interface between the metal base plate and the porous layer was evaluated.

[0287] As the results, a state where almost no exfoliation existed in the interface was indicated by "A," a state where slight exfoliation occurred is indicated by "B," a state where exfoliation occurred in several portions is indicated by "C," and a state where the porous layer was exfoliated when the support was bent is indicated by "D." 2. Preparation of Presensitized Plate

[0288] After a photosensitive coating solution having the undermentioned composition was applied onto any one of the supports for lithographic printing plates obtained in Examples 1 to 22 and Comparative Examples 1 to 3 so that the coating quantity after dried became 1.0g/m^2, the coating was dried at 140°C for 50 seconds in Perfect Oven PH200 (made by Espec Corporation (renamed from Tabai Espec Corporation)) with its Wind Control set at 7. Thus, the presensitized plate was obtained.

(Composition of Photosensitive Coating Solution)

[0289] m, p-cresol novolak (m/p ratio = 6/4, weight average molecular weight: 3,500, containining 0.5 mass% of unreacted cresol): 0.427 g

[0290] Alkali-soluble resin (F-1) including a siloxane structure obtained by the undermentioned synthesis method: 0.047 g

[0291] Specific copolymer 1 described in JP 11-288093 A: 2.37g

[0292] Cyanine dye A represented by the undermentioned formula: 0.155 g

[0293] 2-methoxy-4-(N-phenylamino)benzene: 0.03 g

[0294] Diazonium hexafluorophosphate tetrahydrophthalic anhydride: 0.19 g

[0295] Counter ion of ethyl violet converted into 6-hydroxy-β-naphthalenesulfonic acid: 0.05 g

[0296] Fluoro surfactant (MEGAFAC F-176PF, made by Dainippon Ink and Chemicals, Inc.): 0.035 g

[0297] Fluoro surfactant (DEFENSA MCF-312, made by Dainippon Ink and Chemicals, Inc.): 0.05 g

[0298] p-toluenesulfonic acid: 0.008 g

[0299] Bis-p-hydoxyphenylsulfon: 0.063 g

[0300] n-dodecyl stearylate: 0.06 g

[0301] γ-butyrolactone: 13 g

[0302] Methyl ethyl ketone: 24 g

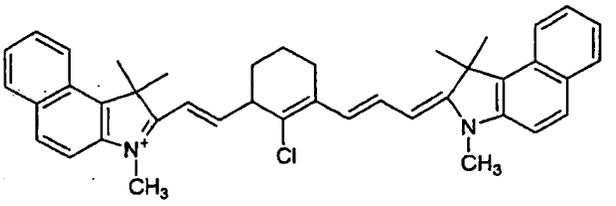
[0303] 1-methoxy-2-propanol: 11 g

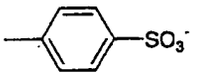
(Synthesis of Alkali-soluble Resin (F-1) including Siloxane structure)

[0304] Cresol novolak (m/p ratio = 6/4, weight average molecular weight = 5,200, 120 g) was dissolved in 400 mL of methanol, 5.4 g of sodium methoxide was added, and the solution was stirred for 30 minutes. Methanol was evaporated under reduced pressure, 400 mL of tetrahydrofuran was added, and the solvent was thus substituted. After adding 17 g of epoxy-type terminal reactive silicone MCR-E11 (made by Chisso Corporation) thereto, the solution was heated for 6 hours and refluxed. The reaction solution was cooled down to a room temperature and then poured into 8,000 mL of water. The separated matter was filtered, rinsed with water and dried, thus obtaining 132 g of the alkali-soluble resin (F-1) including a siloxane structure.

Cyanine dye A

[0305]





3. Evaluation of Presensitized Plate and Lithographic Printing Plate

<Press Life>

[0306] Each presensitized plate obtained as described above was exposed under an output condition of a resolution of 2,400 dpi using Trendsetter 3244VFS (made by Creo, Inc.) equipped with a water cooling-type 40W infrared semiconductor laser.

[0307] After the image exposure, development was performed at a solution temperature of 30°C for a development time of 12 seconds using PS Processor 900H (made by Fuji Photo Film Co., Ltd.) filled with Developer DT-1 (diluted at a ratio of 1/8, made by Fuji Photo Film Co., Ltd.) and Finisher PF2W (diluted at a ratio of 1:1, made by Fuji Photo Film Co., Ltd.). Note that, at this time, the electric conductivity of the developer was 45 mS/cm.

[0308] Next, printing was performed by Mitsubishi Diya F2 printing machine (Mitsubishi Heavy Industries, Ltd.) using DIC-GEOS (s) scarlet ink. After 50 sheets were printed, measurement printing was performed to count how many sheets without residual color, residual layers and scum could be obtained. That is, the printing was terminated when any of residual color, residual layers and scum became under an allowable level as a printed matter, and the number of printed sheets at this point in time was determined as the terminated number of sheets. The results are shown in Table 2.

[0309] In Table 2, a case of 50,000 sheets or more is indicated by "A," a case of less than 50,000 sheets and 30,000 sheets or more is indicated by "B," a case of less than 30,000 sheets and 10,000 sheets or more is indicated by "C," and a case of less than 10,000 sheets is indicated by "D."

Table 2 (No.1)

	Metal Plate No.	Pretreatment								Coating solution No.	Film thickness of Porous layer (μm)	Adhesion	Anti-interfacial exfoliation property	Press life
		Acid/alkali treatment				Anodizing treatment								
		Kind of solution	Concentration (g/l)	Temperature (°C)	Time (Sec.)	Kind of solution	Concentration (g/l)	Temperature (°C)	Time (Sec.)					
Example 1	1	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 2	1	Sulfuric acid	360	60	60	Sulfuric acid	170	33	10	C-1	2	A	A	A
Example 3	1	NaOH	360	70	10	-	-	-	-	-	-	-	-	-
		Sulfuric acid	360	60	60	-	-	-	-	C-1	2	A	A	A
Example 4	1	NaOH	360	70	10	-	-	-	-	-	-	-	-	-
		Sulfuric acid	360	60	60	Sulfuric acid	170	33	10	C-1	2	A	A	A
Example 5	2	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 6	3	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 7	4	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 8	5	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 9	6	Sulfuric acid	360	60	60	-	-	-	-	C-2	2	A	A	A
Example 10	7	Sulfuric acid	360	60	60	-	-	-	-	C-3	2	A	A	A
Example 11	8	Sulfuric acid	360	60	60	-	-	-	-	C-4	2	A	A	-

Table 2 (No.2)

	Metal Plate No.	Pretreatment								Coating solution No.	Film thickness of Porous layer (μm)	Adhesion	Anti-interfacial exfoliation property	Press life
		Acid/alkali treatment				Anodizing treatment								
		Kind of solution	Concentration (g/l)	Temperature (°C)	Time (Sec.)	Kind of solution	Concentration (g/l)	Temperature (°C)	Time (Sec.)					
Example 12	9	Sulfuric acid	360	60	60	-	-	-	-	C-8	2	B	B	B
Example 13	1	Sulfuric acid	360	60	60	-	-	-	-	C-1	2	B	B	B
Example 14	1	Sulfuric acid	360	60	10	-	-	-	-	C-2	2	B	B	B
Example 15	1	Sulfuric acid	360	60	60	-	-	-	-	C-3	2	B	B	B
Example 16	1	Sulfuric acid	360	60	10	-	-	-	-	C-4	2	B	B	B
Example 17	1	Sulfuric acid	360	60	60	-	-	-	-	C-5	2	B	B	B
Example 18	1	Sulfuric acid	360	60	60	-	-	-	-	C-6	2	B	B	B
Example 19	1	Sulfuric acid	360	60	60	-	-	-	-	C-7	2	B	B	B
Example 20	1	Sulfuric acid	360	60	60	-	-	-	-	C-8	2	C	C	C
Example 21	1	Alcohol		Ordinary Temperature	60	Sulfuric acid	170	33	10	C-1	2	B	B	B
Example 22	1	Methyl ethyl ketone		Ordinary Temperature	60	Sulfuric acid	170	33	10	C-1	2	B	B	B
Comparative Example 1	1	-	-	-	-	-	-	-	-	C-1	2	D	D	D
Comparative Example 2	1	Alcohol		Ordinary Temperature	60	-	-	-	-	C-1	2	C	D	D
Comparative Example 3	1	Methyl ethyl ketone		Ordinary Temperature	60	-	-	-	-	C-1	2	C	D	D

[0310] It is found from the results in Table 2 that the support for a lithographic printing plate and the presensitized plate of the present invention which are provided with a specific porous layer and have a specific pretreatment layer between the porous layer and the metal base plate are excellent in adhesion between the base plate and the porous layer and therefore excellent in press life.

[0311] In addition, even when an aluminum plate is used as the base plate, since the porous layer can be formed at a relatively low temperature (less than the softening temperature of aluminum), deterioration in printing performance due to softening of the aluminum plate (particularly a deviation between a plate and an image) is not observed.

[0312] Further, it is found that, even though the support for a lithographic printing plate provided with the porous layer of the present invention is manufactured by using any of the various kinds of base plates, the support is excellent in all of scratch resistance, sensitivity, scum resistance, adhesion, interfacial exfoliation resistance, and press life.

[Effects of the Invention]

[0313] The support for a lithographic printing plate and the sensitized plate of the present invention have the porous layer of specially high adiathermancy, are capable of plate making by scanning exposure base on a digital signal, have scratch resistance, excellent sensitivity, scum resistance and press life, and are excellent in abrasion resistance since the adhesion between the porous layer and the plate is high.

Claims

1. A support for a lithographic printing plate comprising a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom on a surface of a metal base plate subjected to acid or alkali treatment.

2. A support for a lithographic printing plate comprising a porous layer where particles of a metal oxide are bonded by a compound containing a metal atom and a phosphorus atom on a surface of a metal base plate subjected to anodizing treatment.

3. The support for a lithographic printing plate according to claim 1 or 2, wherein the metal oxide is at least one kind of metal oxide or composite oxide selected from the group consisting of silicon, magnesium, zirconium and titanium.

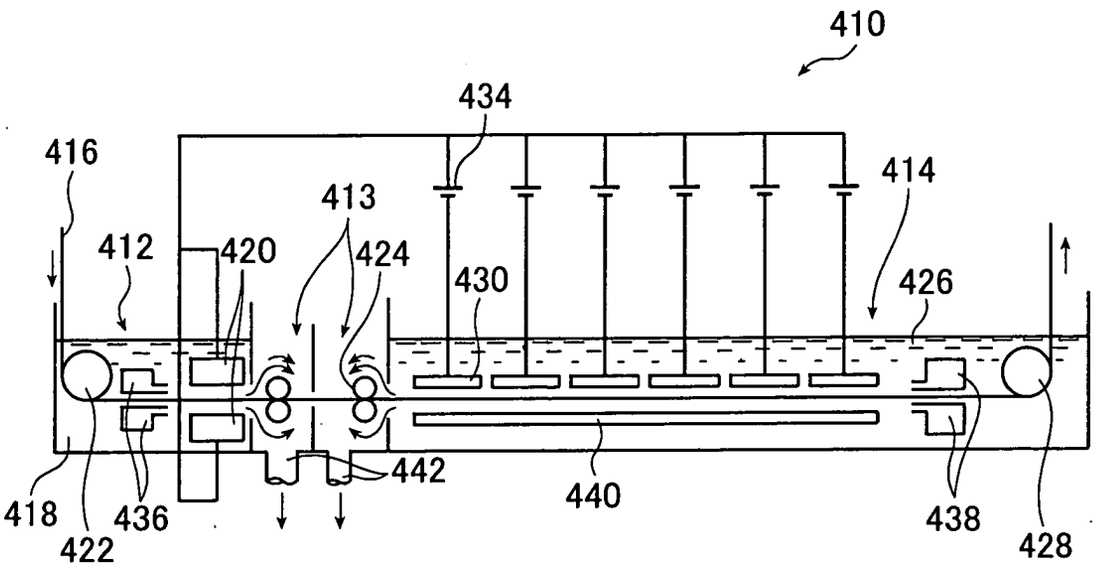
4. The support for a lithographic printing plate according to any one of claims 1 to 3, further comprising a sealing layer on the porous layer.

5. The support for a lithographic printing plate according to claim 4, wherein a porosity of the porous layer is 20% or higher and a porosity of the sealing layer is less than the porosity of the porous layer.

6. The support for a lithographic printing plate according to claim 4 or 5, wherein a film thickness of the porous layer is 0.5 to 20 μm.

7. A presensitized plate comprising an image recording layer on the support for a lithographic printing plate according to any one of claims 1 to 6.

FIG.1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Application Number
EP 04 01 1378

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DE 198 14 877 A (EASTMAN KODAK CO) 22 October 1998 (1998-10-22) * page 2, line 22 - line 39 * * page 3, line 24 - line 28 * * page 4, line 55 - line 60 *	1-7	B41N1/00 B41N1/08 B41N3/00 B41N3/03
X	US 5 249 525 A (LEWIS THOMAS E ET AL) 5 October 1993 (1993-10-05) * column 26, line 23 - line 45 * * column 31, line 67 - line 68 * * column 32, line 23 - line 30 *	1-7	
X	EP 1 302 312 A (FUJI PHOTO FILM CO LTD) 16 April 2003 (2003-04-16) * paragraphs [0039], [0040]; claims 1-6 *	1-7	
X	EP 1 293 579 A (FUJI PHOTO FILM CO LTD) 19 March 2003 (2003-03-19) * paragraphs [0027], [0124], [0289], [0290]; claims 1-3 *	1-7	
X	US 4 647 346 A (MILLER GARY R ET AL) 3 March 1987 (1987-03-03) * column 1, line 66 - column 2, line 21; claim 5 *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B41N
X	US 3 808 000 A (KETLEY A ET AL) 30 April 1974 (1974-04-30) * claim 1; examples 4,5 *	1-7	
X	DATABASE WPI Section Ch, Week 199708 Derwent Publications Ltd., London, GB; Class G05, AN 1997-082475 XP002289610 & JP 08 324144 A (KONICA CORP) 10 December 1996 (1996-12-10) * abstract *	1-7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	23 July 2004	Spyropoulou, E

CATEGORY OF CITED DOCUMENTS

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23-07-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19814877 A	22-10-1998	US 5855173 A	05-01-1999
		DE 19814877 A1	22-10-1998
		JP 10309877 A	24-11-1998
US 5249525 A	05-10-1993	US 4911075 A	27-03-1990
		US 5109771 A	05-05-1992
		US 5165345 A	24-11-1992
		DE 431054 T1	19-12-1991
		EP 0431054 A1	12-06-1991
		JP 4501684 T	26-03-1992
		WO 9002044 A2	08-03-1990
		US 4958563 A	25-09-1990
		US 4947750 A	14-08-1990
		US 4947749 A	14-08-1990
		US 4958562 A	25-09-1990
		US 5005479 A	09-04-1991
		US 5121688 A	16-06-1992
		US 5163368 A	17-11-1992
		US 5161465 A	10-11-1992
		US 5103731 A	14-04-1992
		US 5188032 A	23-02-1993
		US 5148746 A	22-09-1992
		US 5235914 A	17-08-1993
		US 5237923 A	24-08-1993
		US 5262805 A	16-11-1993
		CA 2045167 A1	29-05-1991
		DE 455804 T1	19-03-1992
		EP 0455804 A1	13-11-1991
		JP 2801777 B2	21-09-1998
		JP 5502192 T	22-04-1993
		WO 9108108 A1	13-06-1991
		AT 146126 T	15-12-1996
		CA 2053575 A1	26-08-1992
		DE 69123561 D1	23-01-1997
		DE 69123561 T2	03-07-1997
		EP 0501065 A1	02-09-1992
		JP 2735429 B2	02-04-1998
		JP 4312890 A	04-11-1992
EP 1302312 A	16-04-2003	JP 2003118253 A	23-04-2003
		JP 2003118254 A	23-04-2003
		EP 1302312 A2	16-04-2003
		US 2003138713 A1	24-07-2003
EP 1293579 A	19-03-2003	JP 2003080857 A	19-03-2003
		JP 2003103950 A	09-04-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 01 1378

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-07-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1293579 A		CN 1413838 A	30-04-2003
		EP 1293579 A2	19-03-2003
		US 2003124364 A1	03-07-2003
US 4647346 A	03-03-1987	DE 3671921 D1	19-07-1990
		EP 0218159 A1	15-04-1987
		JP 7067867 B	26-07-1995
		JP 62099198 A	08-05-1987
US 3808000 A	30-04-1974	BE 797180 A1	16-07-1973
		DE 2314295 A1	18-10-1973
		FR 2178622 A5	09-11-1973
		IT 981564 B	10-10-1974
		JP 49008428 A	25-01-1974
		NL 7304014 A	02-10-1973
JP 8324144 A	10-12-1996	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82