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(54) Process for preparing a substrate for a lithographic plate.

(57) A process for preparing a substrate for a lithographic plate, which comprises the steps of subjecting at least one surface of an aluminum plate to a surface roughening treatment, anodizing the resulting plate to form at least 2 g/m^2 of an anodized layer, sealing the anodized plate with hot water or water vapor to reduce the surface area of the anodized layer by from 40 to 95 % and subjecting the sealed plate to at least one of a hydrophilizing treatment or a hydrophilic-undercoating treatment.

A lithographic plate which comprises the substrate prepared by the process of the present invention has excellent strength of non-image areas, corrosion resistance of non-image areas, reproduction of highlight areas, printing durability, little dye staining of non-image areas and non-image areas having high hydrophilicity. Further, the lithographic plate produces prints having little background contamination.

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BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing a substrate for a lithographic plate, particularly a grained aluminum substrate for a lithographic plate.

A presensitized plate (hereinafter referred to as "PS plate") which comprises an aluminum plate and a light-sensitive composition applied thereon in a form of film is generally prepared by subjecting the aluminum plate to surface roughening treatment by mechanical methods such as brush graining and ball graining, electrochemical methods such as electrolytic graining, or a combination thereof, etching and anodizing the resulting plate and optionally hydrophilizing the plate and providing a light-sensitive layer thereon.

The obtained PS plate is generally subjected to an imagewise exposure to light, development, correction and gumming-up to prepare a lithographic plate. The lithographic plate is mounted on a printing press and the printing operation is carried out.

Among numerous properties of a lithographic plate, the strength of non-image areas is improved by thickening the anodized layer in the lithographic plate.

However, when the thickness of the anodized layer is large, in the case of a positive working presensitized plate, the presensitized plate has such disadvantages that dyes and polymeric binders remain in non-image areas after development and reproduction of highlight areas gets worse. In the case of a negative working presensitized plate, the presensitized plate has such disadvantages that dyes and polymeric binders in the light-sensitive layer are irreversibly adsorbed on the surface of a substrate with time to produce stain and reproduction of halftone dots in shadow areas gets worse.

The resistance of non-image areas to acids or alkalis is improved by sealing the anodized layer. There are a number of methods of sealing such as a method comprising the step of immersing the anodized aluminum substrate in an aqueous solution of an alkali metal silicate as disclosed in United States Patent No.3,181,461, a method comprising the step of immersing the anodized aluminum substrate in an aqueous solution of an alkali metal fluorozirconate as disclosed in United States Patent No.3,440,050, and a method comprising the step of treating the anodized aluminum substrate with polyvinl phosphonic acid as disclosed in United States Patent Nos.4,153,461 and 4,689,272. PS plates comprising the substrates prepared by the above methods provide lithographic plates which do not have contamination in non-image areas so that prints obtained thereby have no background contamination. However, the PS plates have the disadvantage of poor printing durability compared with that of PS plates which are not subjected to a treatment as mentioned above.

Japanese Unexamined Patent Publication (hereinafter referred to as J.P.KOKAI) No. Sho 59-114100 discloses a method of treating an anodized aluminum plate with water vapor. Lithographic plates comprising a substrate treated by the above method are considered to have sufficient printing durability. However, if the sealing reaction excessively proceeds, in the case of a positive working presensitized plate, the hydrophilicity of non-image areas is reduced after developing the positive working presensitized plate with a developer comprising silicate as a main component. In the case of a negative working presensitized plate, the hydrophilicity of non-image areas is reduced so that the resulting prints have a lot of background contamination and the printing durability of the resulting lithographic plate is reduced.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a process for preparing a substrate for a lithographic plate which has good strength of non-image areas and excellent corrosion resistance.

Another object of the present invention is to provide a process for preparing a presensitized plate comprising the above substrate.

The aforementioned object of the present invention can effectively be accomplished by providing a process for preparing a substrate for a lithographic plate, which comprises the steps of subjecting at least one surface of an aluminum plate to a surface roughening treatment, anodizing the resulting plate to form at least 2 g/m^2 of an anodized layer, sealing the anodized plate with hot water or water vapor to reduce the surface area of the anodized layer by from 40 to 95 % and subjecting the sealed plate to a hydrophilizing treatment and/or a hydrophilic-undercoating treatment.

DETAILED EXPLANATION OF THE INVENTION

The present invention will hereunder be described in more detail.

(Aluminum Plate)

Examples of the aluminum plate which can be used in the present invention include pure aluminum and aluminum alloy plates which comprise aluminum as a main component and the other atoms in a trace amount. Examples of the other atoms include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, titanium and the like. The ratio of the other atoms to the aluminum alloy may be up to 10 % by weight based on the total weight of the aluminum alloy. Pure aluminum is the most preferred for the substrate of the present invention. However, aluminum alloys containing the least possible amount of the other atoms is preferred because pure alminum can not be easily obtained by refining techniques. Any aluminum alloy which contains some amount of the other atoms can be used as a material of the substrate of the present invention. Thus, any known and/or used aluminum materials such as JIS A1050, JIS A1100, JIS A1200, JIS A3103, JIS A3003 and JIS A3005 can be suitably used in the present invention, but the invention is not limited to specific materials. The thickness of the aluminum plate is preferably from about 0.1 mm to about 0.5 mm.

(Surface Roughening Treatment)

Prior to graining, an aluminum plate can optionally be treated to remove rolling oil from the surface of the plate, for example, by a degreasing treatment with a surfactant or an alkaline aqueous solution. An aluminum plate is grained by various methods. Examples of the graining methods include a mechanical method of roughening the surface of the aluminum plate, an electrochemical method of etching the surface of the aluminum plate and a chemical method of selectively etching the surface of the aluminum plate. Examples of the mechanical methods include conventional methods such as ball graining, brush graining, blast graining, buff graining and the like. Examples of the electrochemical methods include a method of applying an alternating or a direct current to the plate in a hydrochloric acid or a nitric acid electrolyte. A combination of the above can be used as described in J.P. KOKAI No. Sho 54-63902.

The aluminum plate thus grained preferably has a surface roughness (center line average roughness) of from 0.3 to 1.0μ , more preferably from 0.3 to 0.8μ .

The aluminum plate thus grained is optionally etched with an alkaline etching agent and then neutralized.

(Anodization)

The aluminum plate thus treated is subsequently anodized.

Any electrolyte can be used in anodizing the aluminum plate as long as a porous anodized layer can be obtained. In general, sulfonic acid, phosphoric acid, oxalic acid, chromic acid or mixtures thereof; sodium hydroxide, potassium hydroxide, or mixtures thereof; or ammonium fluoride-containing bath can be used as an electrolyte. The concentration of the electrolyte can be suitably modified depending on the kind of the electrolyte.

Generally, anodization can be suitably carried out under conditions of an electrolyte concentration of from 1 to 80 % by weight, a solution temperature of from 5 to 80 °C , a current density of from 5 to 80 A/dm^2, a voltage of from 1 to 100V and a time of from 5 seconds to 10 minutes. The conditions can be modified depending on the electrolyte to be used.

Preferred is anodization using sulfuric acid as an electrolyte, especially under the conditions as disclosed in British Patent No. 1,412,768 or United States Patent No. 4,211,619.

Most preferred anodization using an electrolyte comprising from 5 to 20 % by weight of sulfuric acid and from 3 to 15 % by weight of aluminum ions at a temperature of from 25 to 50°C with a direct current having a current density of from 5 to 20 A/dm^2.

The amount of the anodized layer is preferably from 2 to 5 g/m^2.

(Sealing)

Sealing is a treatment of sealing pores in the porous anodized layer with a metal, oxide or hydroxide. In the present invention, sealing is carried out by exposing a porous anodized layer to a vapor atmosphere or immersing it in hot water.

When sealing is carried out with vapor, water vapor under elevated or normal pressure is used. Sealing with vapor under normal pressure can be suitably carried out under conditions of a relative humidity of not less than 70 % and a vapor temperature of not less than 95°C for from 2 seconds to 2 minutes.

When sealing is carried out by immersing the anodized layer in hot water, various additives which can promote sealing are preferably added to the hot water.

A sealing ratio is herein used as an indicator of the degree of sealing. The sealing ratio represents a reducing ratio of the surface area of an anodized layer, and it is defined by the following equation:

$$\text{Sealing ratio (\%)} = \frac{S_0 - S}{S_0} \times 100$$

wherein S_0 is the surface area before sealing and S is the surface area after sealing.

The surface area of an anodized layer is reduced by a sealing ratio of from 40 to 95 %, preferably from 60 to 90 % by sealing.

The surface area is determined by a simple BET type QUANTASORB (available from Uasa Ionics Co.,Ltd).

The aluminum plate thus sealed can be used as a substrate for a lithographic plate. For example, the sealed plate can be used as a substrate for a wipe-on plate or that for a presensitized plate by further applying a light-sensitive layer suitable for lithography thereon. In the present invention, the sealed aluminum plate is preferably further subjected to a hydrophlizing treatment, an application of a hydrophilic undercoating layer and the like, alone or in combination.

(Hydrophilizing Treatment)

Hydrophilizing treatments used in the present invention include any known methods such as methods of treating an aluminum plate with alkali metal silicates such as sodium silicate as disclosed in United States Patent Nos. 2,714,066 and 3,181,461, a method of treating an aluminum plate with potassium fluorozirconate as disclosed in Japanese examined patent publication (hereinafter referred to as J.P. KOKOKU) No. Sho 36-22063 and a method of treating an aluminum plate with polyvinyl phosphonic acid as disclosed in United States Patent Nos. 4,153,461 and 4,689,272. Such a hydrophilizing treatment is desired especially when a light-sensitive layer comprising a diazo resin is applied on the aluminum substrate.

(Hydrophilic Undercoating)

Preferred hydrophilic undercoatings used in the present invention include a hydrophilic layer comprising a compound having at least one amino group and at least one group selected from the group consisting of carboxyl, carboxylate, sulfo and sulfonate, as disclosed in J.P. KOKAI No. Sho 60-149491; a hydrophilic layer comprising a compound having at least one amino group and at least one hydroxy group, as disclosed in J.P. KOKAI No. Sho 60-232998; a hydrophilic layer comprising phosphate disclosed in J.P. KOKAI No. Sho 62-19494; and a hydrophilic layer comprising a polymeric compound having at least one monomer unit having sulfo group as a repeating unit in the molecule, as disclosed in J.P. KOKAI No. Sho 59-101651. The undercoating may be applied after sealing or after sealing and the above hydrophilizing treatment.

The anodized aluminum plate may be treated with an aqueous solution of an alkali metal silicate as disclosed in United States Patent No. 3,181,461 before or after applying the above intermediate undercoating thereon.

If a presensitized plate has a light-sensitive layer on only one of the two surfaces of an aluminum plate (hereinafter referred to as "one-side PS plate"), the above explained surface treatments may be carried out on one of the two surfaces of the aluminum plate, to which a light-sensitive layer is applied (hereinafter referrred to as "right-side surface"). If a presensitized plate has light-sensitive layers on both of the two surfaces of an aluminum plate (hereinafter referred to as "both-side PS plate"), the above explained surface treatments must be carried out on both of the two surfaces of the aluminum plate.

When the aluminum plate of a one-side PS plate is anodized, anodized layers (anodic oxide layers) are generally formed on both of the two surfaces of the aluminum plate. It is difficult to selectively anodize only one of the two surfaces of the aluminum plate, if the aluminum plate is not subjected to any special treatments before anodization, such as applying a protective insulating coating to the one of the two surfaces of the aluminum plate, to which a light-sensitive layer is not applied (hereinafter referred to as "back-side surface"). The amount of the anodized layer formed on the back-side surface is generally from 0.05 to 1.5 g/m^2. The amount can be controlled to be from 0.05 to 1.0 g/m^2 by anodizing an aluminum plate while setting up an insulating sheet or plate near the back-side surface of the aluminum plate in an anodic oxidizing bath as disclosed in J.P.KOKAI No. Sho 57-47894 and DE-A 3135747. If a PS plate comprising an aluminum plate which has an anodized layer on the back-side surface is developed with an aqueous alkaline developer, especially that having pH at least 12, the anodized layer of the backside surface is dissolved in the developer so that the developer is exhaused and sludge-like insolubles are produced in an early stage. As a result, the lifetime of the developer is reduced.

The above mentioned problems can be greatly reduced by sealing the anodic layer of the back-side surface of the aluminum plate to reduce the surface area thereof by at least 80 %, preferably at least 90 %. Such sealing can be carried out in any known methods, preferably in the same method as that of sealing the right-side surface of the aluminum plate.

Any known light-sensitive layer is applied to the substrate thus obtained to obtain a presensitized plate. A lithographic plate which is obtained by processing the presensitized plate has excellent properties.

Any composition can be used in the light-sensitive layer as long as solubility or swellability thereof in a developer is changed after exposure to light. Representative examples are explained hereinafter.

(A) Light-sensitive Layer comprising O-Quinonediazide

Examples of the positive working light-sensitive compounds include o-quinonediazide compounds and the typical examples thereof include o-naphthoquinonediazide compounds.

Preferred examples of the o-quinonediazide compounds include an ester of 1,2-naphthoquinone (2) diazide-5-sulfonyl chloride and a pyrogallol-acetone resin, as disclosed in J.P.KOKOKU No. Sho 43-28403-(U.S.Patent No. 3,635,709). Other preferred examples of the o-quinonediazide compounds include an ester of 1,2-naphthoquinone (2) diazide-5-(or -4-)-sulfonyl chloride and a phenol-formaldehyde resin, as disclosed in U.S.Patent Nos. 3,046,120 and 3,188,210. Other useful examples of the o-quinonediazide compounds include those disclosed in many patent publications, for example, such as J.P.KOKAI Nos. Sho 47-5303, Sho 48-63802, Sho 48-63803, Sho 48-96575, Sho 49-38701, Sho 48-13354, Sho 51-139402, Sho 58-150948, Sho 58-203434, Sho 59-165053, Sho 60-121445, Sho 60-134235, Sho 60-163043, Sho 61-118744, Sho 62-10645, Sho 62-10646, Sho 62-153950, Sho 62-178562 and Sho 64-76047; J.P.KOKOKU Nos. Sho 37-18015, Sho 41-11222, Sho 45-9610 and Sho 49-17481; U.S.Patent Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495, 3,785,825, 3,102,809, 3,126,281, 3,130,047, 3,148,983, 3,184,310, 3,188,210 and 4,639,406; G.B.Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932; and German Patent No. 854,890.

O-Naphthoquinonediazide compounds especially preferred in the present invention are those obtained by a reaction of a polyhydroxy compound having a molecular weight of not greater than 1,000 and 1,2-diazonaphthoquinone sulfonic chloride. Illustrative examples of the above compounds include those disclosed in J.P. KOKAI Nos. Sho 51-139402, Sho 58-150948, Sho 58-203434, Sho 59-165053, Sho 60-121445, Sho 60-134235, Sho 60-163043, Sho 61-118744, Sho 62-10645, Sho 62-10646, Sho 62-153950, Sho 62-178562 and Sho 64-76047; and United States Patent Nos. 3,102,809, 3,126,281, 3,130,047, 3,148,983, 3,184,310, 3,188,210 and 4,639,406.

Preferably, o-naphthoquinone diazide compounds are prepared by reacting from 0.2 to 1.2, more preferably, from 0.3 to 1.0 equivalent of 1,2-naphthoquinone (2) diazide-5-(or -4-) sulfonyl chloride with 1 equivalent of a hydroxyl group of a polyhydroxy compound. As the 1,2-diazonaphthoquinone sulfonic acid, 1,2-diazonaphthoquinone-5-sulfonic cloride is preferred. Further, 1,2-diazonaphthoquinone-4-sulfonic chloride can be used.

O-Naphthoquinonediazide compounds thus obtained are a mixture of compounds wherein 1,2-diazonaphthoquinone sulfonic ester groups are introduced in different amounts at different positions. The amount of compounds whose hydroxyl groups are all converted into 1,2-dizonaphthoquinone sulfonic esters, that is, the amount of the compound which is completely esterified, is preferably not less than 5 mole %, more preferably from 20 to 99 mole %.

Polymers having ortho-nitrocarbinol ester groups, which are disclosed in J.P.KOKOKU No. 56-2696(U.S. Patent No. 3,849,137), can be used as positive working light-sensitive compounds instead of the o-naphthoquinonediazide compounds.

Further, combinations of compounds which generate acids photolytically and compounds having -C-O-C- or -C-O-Si groups which are dissociated by acids can be used in the light-sensitive compounds of the PS plate of the present invention.

Examples of such combinations include combinations of compounds which generate photolytically acids and acetal or O,N-acetal compounds (J.P.KOKAI No. Sho 48-89003)(U.S. Patent No. 3,779,778); orthoester or amideacetal compounds (J.P.KOKAI No. Sho 51-120714)(U.S. Patent No. 4,101,323); polymers which have acetal or ketal groups on the main chain (J.P.KOKAI No. Sho 53-133429)(U.S. Patent No. 4,247,611); enolester compounds (J.P.KOKAI No. Sho 55-12995)(U.S. Patent No. 4,248,957); N-acylimino carbon compounds (J.P.KOKAI No. Sho 55-126236) (U.S. Patent No. 4,250,247); polymers which have orthoester groups on the main chain (J.P.KOKAI No. Sho 56-17345)(U.S. Patent No. 4,311,782); silylester compounds (J.P.KOKAI No. Sho 60-10247)(U.S. Patent No. 4,752,552); or silylether compounds (J.P.KOKAI Nos. Sho 60-37549 and Sho 60-121446)(U.S. Patent No. 4,816,375) and the like.

The amount of the o-quinonediazide compounds (including combinations illustrated above) is preferably from 10 to 50% by weight and more preferably 15 to 40% by weight based on the total weight of the light-sensitive composition.

These o-quinonediazide compounds may be used alone, but are preferably used as a mixture with an alkali-soluble resin which functions as a binder. Preferred examples of the alkali-soluble resins include alkali-soluble novolak resins. Examples of the alkali-soluble novolak resins include a cresol-formaldehyde resin such as a phenol-formaldehyde resin, a m-cresol-formaldehyde resin, a p-cresol-formaldehyde resin, a m-/p-cresol-formaldehyde resin, a phenol/cresol-(including m-, p-, or m-/p- copolycondensed) formaldehyde resin; a phenol modified xylene resin; polyhydroxystyren e; polyhalogenated hydroxystyrene; an acrylic resin having phenolic hydroxyl groups, such as those disclosed in J.P.KOKAI No. Sho 51-34711; an acrylic resin having sulfonamide groups, as disclosed in J.P.KOKAI No. Hei 2-866; an urethane resin and the like. The weight-average molecular weight of the alkali-soluble polymer is preferably from 500 to 20,000 and the number-average molecular weight thereof is preferably from 200 to 60,000.

The alkali-soluble polymer can be used in an amount of less than 70 % by weight based on the total weight of the light-sensitive composition.

Further, a condensation product of phenol which has alkyl groups having from 3 to 8 carbon atoms as substituents and formaldehyde, such as a t-butylphenol-formaldehyde resin and an octylphenol-formaldehyde resin, can be preferably added to the positive working light-sensitive composition in order to improve the ink receptivity of the image areas.

The light-sensitive composition used in the PS plate of the present invention may further contain cyclic acid anhydrides for improving sensitivity of the PS plate; agents or compositions for obtaining a visible image immediately after imagewise exposure to light; dyes as image colorants; fillers and the like.

Examples of the cyclic acid anhydrides include phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, 3,6-endoxy- Δ^4-tetrachloro phthalic anhydride, tetrachloro phthalic anhydride, maleic anhydride, chloro maleic anhydride,α -phenyl maleic anhydride, succinic anhydride, pyromellitic anhydride and the like, all of which are disclosed in U.S.Patent No. 4,115,128. Sensitivity can become up to about 3 times higher by adding from 1 to 15 % by weight of the cyclic acid anhydrides based on the total weight of the light-sensitive composition.

Typical examples of the agents for obtaining a visible image immediately after imagewise exposure to light as a salt-forming organic dye include combinations of light-sensitive compounds which releases an acid upon exposure to light and salt-forming organic dyes. More specifically, examples of the combinations include combinations of o-naphthoquinonediazide-4-sulfonyl halide and salt-forming organic dye disclosed in J.P.KOKAI Nos. Sho 50-36209(U.S. Patent No. 3,969,118) and Sho 53-8128 and combinations of trihalomethyl compounds and salt forming organic dyes disclosed in J.P.KOKAI Nos. Sho 53-36223(U.S. Patent No. 4,160,671), Sho 54-74728(U.S. Patent No. 4,232,106), Sho 60-3626, Sho 61-143748, Sho 61-151644 and Sho 63-58440.

Dyes other than the above salt-forming organic dyes can be used as colorants of the image. Preferred examples of the dyes including salt-forming organic dyes include oil-soluble dyes and basic dyes. More specifically, examples of such dyes include Oil Yellow # 101, Oil Yellow # 130, Oil Pink # 312, Oil Green BG, Oil Blue BOS, Oil Blue # 603, Oil Black BY, Oil Black BS, Oil Black T-505 (available from Orient Chemical Industry Co.), Victoria Pure Blue, crystalviolet (CI42555), methylviolet (CI42535), rhodamine B (CI45170B), malachite green (CI42000), methylene blue (CI52015) and the like. A dye disclosed in J.P.KOKAI No. Sho 62-293247 is especially preferred.

The light-sensitive composition is dissolved in a solvent which dissolves each of the above components and is applied on the substrate to prepare a PS plate. Examples of the solvents include ethylene dichloride, cyclohexanone, methyl ethyl ketone, ethyleneglycol-mono-methylether, ethyleneglycol-mono-ethylether, 2-methoxyethyl acetate, 1-methoxy-2-propanol, 1-methoxy-2-propylacetate, toluene, ethyl acetate, methyl lactate, ethyl lactate, dimethyl sulfoxide, dimethyl acetamide, dimethyl formamide, water, N-methyl pyrrolidone, tetrahydrofurfuryl alcohol, acetone, diacetone alcohol, methanol, ethanol, isopropanol, diethyleneglycol-dimethylether, a mixture thereof, and the like.

The solid concenration of the above light-sensitive composition is from 2 to 50 % by weight. The amount of the coating can be modified depending on use. For example, the preferred amount of the coating of the light-sensitive composition for a presensitized plate is generally from 0.5 to 3.0 g/m^2. As the amount of the light-sensitive composition decreases, the photosensitivity of the PS plate becomes higher but physical properties of the light-sensitive film becomes lower.

The light-sensitive composition used in the PS plate of the present invention may furthermore contain surfactants, such as fluorine-atom-containing surfactants such as those disclosed in J.P. KOKAI No. Sho 62-170950(U.S. Patent No. 4,822,713), in order to improve coating properties. The ratio of the surfactant to the light-sensitive composition is preferably from 0.01 to 1 % by weight, more preferably from 0.05 to 0.5 % by weight based on the total weight of the light-sensitive composition.

(B)Light-Sensitive Layer comprising a Diazo Resin and a Binder

As negative working light-sensitive diazo compounds, condensation products, that is, light-sensitive resins obtained by condensing formaldehyde with a diphenylamine-p-diazonium salt, which salt is a product of a reaction of a diazonium salt with an organic condensation agent having a reactive carbonyl group such as aldol and acetal. The diazo compounds disclosed in United States Patent Nos. 2, 063,631 and 2,667,415 are preferably used. The other useful condensed diazo compounds are disclosed in J.P. KOKOKU Nos. Sho 49-48001, Sho 49-45322 and Sho 49-45323. These light-sensitive diazo compounds are usually obtained as water-soluble inorganic salts, which enables the compounds to be coted in aqueous solutions thereof. These water-soluble diazo compounds can be reacted with aromatic or aliphatic compounds having at least one phenolic hydroxy group, sulfonic group or a combination thereof in a manner disclosed in J.P.KOKAI No. Sho 47-1167 to obtain reaction products, substantially water-insoluble light-sensitive diazo resins which can be used in the light-sensitive layer.

These water-soluble diazo compounds can be used in the form of hexafluoro phosphates or tetrafluoro borates as disclosed in J.P.KOKAI No. Sho 56-121031.

Examples of reaction products having a phenolic hydroxy group include hydroxy benzophenones, 4,4-bis(4'-hydroxyphenyl)pentanic acid, resorcinol and substituted or unsubstituted diphenolic acids such as diresorcinol. Hydroxy benzophenones include 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxy benzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2,2',4,4'-tetrahydroxy benzophenone. Examples of the preferred sulfonic acids include aromatic sulfonic acids such as sulfonic acids of benzene, toluene, xylene, naphthalene, phenol, naphtol and benzophenone and soluble salts thereof including ammonium or alkali metal salts. The sulfonic group-containing compounds may be generally substituted with lower alkyl, nitro, halo and/or another sulfonic group. Preferred examples of the above compounds include benzene sulfonic acid, toluene sulfonic acid, naphthalene sulfonic acid, 2,5-dimethylbenzene sulfonic acid, sodium benzene sulfonate, naphthalene-2-sulfonic acid, 1-naphthol-2(or 4)-sulfonic acid, 2,4-dinitro-1-naphthol-7-sulfonic acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, sodium m-(p'-anilinophenylazo) benzene sulfonate, alizarin sulfonic acid, o-toluidine-m-sulfonic acid and ethane sulfonic acid. Further, sulfonic esters of alcohols and salts thereof are useful. Generally, these compounds are easily-available as anionic surfactants. Examples of these compounds include ammonium or alkali metal salts of lauryl sulfate, alkylaryl sulfate, p-nonylphenyl sulfate, 2-phenylethyl sulfate, isooctylphenoxy diethoxyethyl sulfate.

These substantially water-insoluble light-sensitive diazo resins are isolated as precipitates by mixing water-soluble light-sensitive diazo resins with, preferably, an aqueous solution of the above aromatic or aliphatic compounds in the same amount as that of the diazo resin.

Diazo resins disclosed in British Patent No. 1,312,925 are also preferred.

Further, diazo resins having oxyacid of phosphorus as disclosed in Japanese patent application Hei. 2-53101; diazo resins condensed with aldehyde having carboxy group or acetal thereof disclosed in Japanese patent application Hei. 1-130493; diazo resins co-condensed with an aromatic compound having carboxy group such as phenoxy acetic acid disclosed in Japanese patent application Hei. 2-40690 are preferred.

The most preferred diazo resin is 2-methoxy-4-hydroxy-5-benzoylbenzene sulfonate of a condensation product of p-diazodiphenylamine and formaldehyde.

The light-sensitive layer suitably comprises the diazo resin in an amount of from 5 to 50 % by weight based on the total weight of the light-sensitive layer. As the amount of the diazo resin decreases, the photosensitivity of the light-sensitive layer increases and the storage stability thereof decreases. The optimum amount of the diazo resin is from about 8 to 20 % by weight.

Various polymeric compounds can be used as binders. Polymeric compounds having hydroxy, amino, carboxy, amide, sulfonamide, active methylene, thioalcohol and epoxy groups are preferred. Examples of the preferred binders include Shellac disclosed in British Patent No. 1,350,521; polymers having a main repeating unit of hydroxyethyl acrylate or hydroxyethyl methacrylate disclosed in British Patent No. 1,460,978 and United States Patent No. 4,123,276; polyamide resins disclosed in United States Patent No. 3,751,257; phenol resins such as polyvinyl formal resin, as disclosed in British Patent No. 1,074,392; polyvinyl acetal resins such as polyvinyl butyral; linear polyurethane resins as disclosed in United States Patent No. 3,660,097; phthalate resins of polyvinylalcohol; an epoxy resin which is a condensation product of bisphenol A and epichlorohydrin; amino-containing polymers such as polyaminostyrene and polyalkylamino(meth) acrylate; and cellulose derivatives such as cellulose acetate, cellulose alkylether, and cellulose acetate phthalate.

The composition comprising the diazo resin and the binder may further comprise a pH indicator as disclosed in British Patent No. 1,041,463, additives such as phosphoric acid and dyes as disclosed in United States Patent No. 3,236,646.

(C)Light-Sensitive Layer comprising an Azide Compound and a Polymeric Compound Binder

Compositions comprising azide compounds and water- or alkali-soluble polymeric compounds, which are disclosed in British Patent Nos. 1,235,281 and 1,495,861, J.P. KOKAI Nos. Sho 51-32331 and Sho 51-36128, can be used. Further, compositions comprising polymers having an azide group and polymeric compounds as binders, as disclosed in J.P. KOKAI Nos. Sho 50-5102, Sho 50-84302, Sho 50-84303 and Sho 53-12984 can be used.

(D)The other Light-Sensitive Resin Layer

Polyester compounds disclosed in J.P. KOKAI No. Sho 52-96696; polyvinyl cinnamate resins disclosed in British Patent Nos. 1,112,277, 1,313,390, 1,341,004 and 1,377,747; and photopolymerizable polymer compositions disclosed in United States Patent Nos. 4,072,528 and 4,072,527 can be used.

(E)Electrophotographic Photosensitive Layer

An electrophotographic photosensitive layer comprises mainly a photoconductive compound and a binder. Optionally, the electrophotographic photosensitive layer may further comprise known pigments, dyes, chemical sensitizing agents, and fillers in order to improve the sensitivity or obtain sensitivity in the desired wavelength range of light. The photosensitive layer may comprise a single layer or two layers which have the function of charge generation or charge transfer. A lithographic plate can be obtained by a known electrophotographic process comprising the steps of forming toner images on a photosensitive layer to use as a resist layer, and decoating the non-image areas. Such processes are disclosed in J.P.KOKOKU Nos. Sho 37-17162, Sho 38-6961, Sho 59-36259 and Sho 59-25217; and J.P.KOKAI Nos. Sho 56-107246, Sho 60-254142, Sho 56-146145, Sho 62-194257, Sho 57-147656, Sho 58-100862 and Sho 57-161863.

The thickness of the light-sensitive layer is from 0.1 to 30μ m, preferably from 0.5 to 10μ m. The solid amount of the light-sensitive layer applied on the substrate is from about 0.1 to about 7 g/m^2, preferably from 0.5 to 4 g/m^2. The presensitized plate is imagewise exposed and then subjected to treatments including development to form images with resin.

For example, in a positive working presensitized plate comprising light-sensitive layer (A), the PS plate is imagewise exposed and then developed with an aqueous alkali solution as disclosed in United States Patent No. 4,259,434 to remove the light-sensitive layer in exposed areas, resulting in a lithographic plate.

In a negative working presensitized plate comprising light-sensitive layer (B), the PS plate is imagewise exposed, and then developed with a developer as disclosed in United States Patent No. 4,186,006 to remove a light-sensitive layer in unexposed areas, resulting in a lithographic plate.

The process of the present invention does not have the disadvantages in the prior art due to the increase in the amount of the anodized layer and sealing of the anodized layer with hot water or water vapor.

The lithographic plate comprising the substrate obtained by the process of the present invention has excellent strength of non-image areas and the excellent corrosion resistance compared with the prior art.

The present invention will hereunder be explained in more detail with reference to the following non-limiting working Examples. Percentages of the Examples are by weight unless otherwise indicated.

Example 1

The surface of JISA 1050 aluminum sheet was grained using a rotating nylon brush and 400-mesh pumice-water suspension. The surface roughness (center line average roughness) of the resulting plate was 0.5μ m. After being washed, the surface of the plate was etched by immersing the plate in 10 % aqueous solution of sodium hydroxide maintained at 70 ° C to dissolve 6 g/m^2 of aluminum. Then the etched plate was washed with water, neutralized by immersing the plate in 20 % aqueous nitric acid solution for 1 minute, and fully washed with water. Thereafter, the plate was subjected to an electrolytic roughening treatment in 0.7 % aqueous nitric acid solution, using alternating waveform current of a sinusoidal waveform, with an anodic voltage of 13 V and a cathodic voltage of 6 V, for 20 seconds. The plate was subsequently immersed in 20 % sulfuric acid solution maintained at 50 ° C to wash the surface of the plate and then washed with water.

The plate was further anodized in 20 % aqueous sulfuric acid solution maintained at 35 ° C to form a porous anodized layer. The anodization was carried out with a current density of 5 A/dm^2 by controlling anodization time to form an anodized layer of 4.0 g/m^2. The substrate thus obtained was sealed in a chamber saturated with vapor at 100 ° C under 1 atmosphere for 10 seconds to form substrate I having a sealing ratio of 60 %.

Solution A comprising 1 g of β -alanine, 5 g of water and 94 g of methanol was applied to substrate I to form 20 mg/m^2 of dry coating and then the substrate was dried at 80 ° C for 30 minutes. The substrate thus prepared was coated with a light-sensitive composition having the following formula to form 2.5 g/m^2 of dry coating and then dried to form a light-sensitive layer.

Light-sensitive Composition

Ester compound of naphthoquinone-1,2-diazide-5-sulfonyl chloride and pyrogallol-acetone resin (disclosed in Example 1 of United States Patent No. 3,635,709)	0.75g
Cresol novolak resin	2.00g
OILBLUE #603 (available from ORIENT CHEMICAL INDUSTRY Co.,Ltd)	0.04g
Ethylene dichloride	16 g
2-Methoxyethyl acetate	12 g

The above prepared presensitized plate was imagewise exposed in a vaccum frame, through a positive transparency, to light from a 3 kW metal halide lamp at a distance of 1 m for 50 seconds. Then the exposed plate was developed with 5.26 % aqueous solution of sodium silicate (pH = 12.7) having a 1.74 molar ratio of SiO_2/Na_2O.

After being developed, the plate was fully washed with water, gummed up and subjected to printing in a usual manner. ① Strength of non-image areas, ② corrosion resistance of non-image areas, ③ dye stains on non-image areas, ④ reproduction of highlight areas, ⑤ hydrophilicity after development and ⑥ printing durability were estimated. The results are shown in Table 1.

Example 2

The procedures of Example 1 were repeated except that the amount of an anodized layer was 2.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 ° C under 1 atmosphere for 6 seconds to form a substrate having a 40 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 1.

Example 3

The procedures of Example 1 were repeated except that the amount of the anodized layer was 5.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 ° C under 1 atmosphere for 15 seconds to form a substrate having a 95 % sealing ratio. The printing properties of the obtained lithographic plate were shown in Table 1.

Example 4

The procedures of Example 1 were repeated except that the sealed plate was immersed in 1 % aqueous solution of polyvinyl phosphonic acid maintained at 60 °C for 1 minute instead of applying the undercoating of β -alanine to the sealed plate. The printing properties of the obtained lithographic plate are shown in Table 1.

Example 5

The procedures of Example 1 were repeated except that the amount of the anodized layer was 6.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 10 seconds to form a substrate having a 60 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 1.

Example 6

The procedures of Example 1 were repeated except that solution B comprising 1 g of phenyl phosphonic acid, 5 g of water and 94 g of methanol was applied to the sealed plate to form 20 mg/m^2 of dry coating instead of applying the undercoating of β -alanine to the sealed plate. The printing properties of the obtained lithographic plate are shown in Table 1.

Comparative Example 1

The procedures of Example 1 were repeated except that the undercoating of β -alanine was not applied to the sealed plate. The printing properties of the obtained lithographic plate are shown in Table 1.

Comparative Example 2

The procedures of Example 1 were repeated except that the amount of the anodized layer was 1.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 10 seconds to form a substrate having a 60 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 1.

Comparative Example 3

The procedures of Example 1 were repeated except that the sealing was not carried out. The printing properties of the obtained lithographic plate are shown in Table 1.

Comparative Example 4

The procedures of Example 1 were repeated except that the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 2 minutes to form a substrate having a 100 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 1.

Example 7

Substrate I was immersed in 2.5 % aqueous solution of No. 3 sodium silicate at 10 °C for 30 minutes, washed with water and dried. The substrate thus-obtained was coated with a light-sensitive composition having the following formula to form 2.0 g/m^2 of dry coating and dried to form a light-sensitive layer.

Light-sensitive Composition

N-(4-Hydroxyphenyl)methacrylamide/2-hydroxyethylmethacrylate/acrylonitrile/methylmethacrylate/methacrylic acid (=15:10:30:38:7 mole ratio) copolymer (average molecular weight 60000)	5.0 g
Hexafluorophosphate of a condensate of 4-diazodiphenyl-amine with formaldehyde	0.5 g
Phosphorous acid	0.05g
Victoria Pure Blue-BOH (available from Hodogaya Chemical Co.,Ltd)	0.1 g
2-Methoxyethanol	100 g

The above-prepared presensitized plate was imagewise exposed in a vaccum frame, through a negative transparency, to light from a 3 kW metal halide lamp at a distance of 1 m for 50 seconds. Then the exposed plate was developed with a developer having the following formula and gummed up with an aqueous solution of gum arabic to obtain a lithographic plate. The lithographic plate was subjected to printing in a usual manner.

Developer

Sodium sulfite	5 g
Benzyl alcohol	30 g
Sodium carbonate	5 g
Sodium isopropylnaphthalene sulfonate	12 g
Purified water	1000 g

① Strength of non-image areas, ② stains caused by irreversible adsorption of the light-sensitive composition and the polymeric binder on the substrate surface with time, ③ reproduction of half tone dots in shadow areas, ④ hydrophilicity of non-image areas and ⑤ printing durability were estimated. The results are shown in Table 2.

Example 8

The procedures of Example 7 were repeated except that the amount of the anodized layer was 2.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 6 seconds to form a substrate having a 40 % sealing ratio. The results after printing are shown in Table 2.

Example 9

The procedures of Example 7 were repeated except that the amount of the anodized layer was 5.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 15 seconds to form a substrate having a 95 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 2.

Example 10

The procedures of Example 7 were repeated except that the amount of the anodized layer was 6.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 10 seconds to form a substrate having a 60 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 2.

Comparative Example 5

The procedures of Example 7 were repeated except that the amount of the anodized layer was 1.0 g/m^2 and the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 10 seconds to form a substrate having a 60 % sealing ratio. The printing properties of the obtained lithographic plate are shown in Table 2.

Comparative Example 6

The procedures of Example 7 were repeated except that the sealing was not carried out. The printing properties of the obtained lithographic plate are shown in Table 2.

Comparative Example 7

The procedures of Example 7 were repeated except that the anodized plate was sealed in a chamber saturated with vapor at 100 °C under 1 atmosphere for 2 minutes to form a substrate having a 100 % sealing ratio. The printing properties of the obtained lithographic plate were shown in Table 2.

Example 11

The surface of JISA 1050 aluminum sheet was grained using a rotating nylon brush and a pumice-water suspension. The surface roughness (center line average roughness) of the resulting plate was 0.5 μ m. After being washed, the surface of the plate was etched by immersing the plate in 10 % aqueous solution of sodium hydroxide maintained at 70 °C to dissolve 6 g/m^2 of aluminum. Then the etched plate was washed with water, neutralized by immersing the plate in 30 % aqueous nitric acid solution for 1 minute, and fully washed with water. Thereafter, the plate was subjected to an electrolytic roughening treatment in 0.7 % aqueous nitric acid solution, using alternating waveform current of a sinusoidal waveform, with an anodic voltage of 13 V and a cathodic voltage of 6 V, for 20 seconds. The plate was subsequently immersed in 20 % sulfuric acid solution maintained at 50 °C to wash the surface of the plate and then washed with water.

The plate was further anodized with a direct current in 20 % aqueous sulfuric acid solution to form a porous anodized layer. The anodization was carried out with a current density of 5 A/dm^2 by controlling anodization time and setting out a polyvinyl chloride plate having a thickness of 10 mm at a distance of 15 mm from the back-side surface of the aluminum plate in the same manner as that disclosed in Example 1 of J.P.KOKAI No. Sho 57-47894 to form an anodized layer of 2.5 g/m^2 on the right-side surface of the aluminum plate and an anodized layer of 0.5 g/m^2 on the back-side surface of the aluminum plate. The substrate thus obtained was sealed with vapor generated in a boiling system at a vapor temperature of 100 °C and 70 % relative humidity for 30 seconds to form substrate having a sealing ratio of 85 % regarding the anodized layer on the right-side surface and a sealing ratio of 95 % regarding the anodized layer on the back-side surface.

Solution A comprising 1 g of β -alanine, 5 g of water and 94 g of methanol was applied to the above obtained substrate to form 20 mg/m^2 of dry coating and then the substrate was dried at 80 °C for 30 minutes. The substrate thus prepared was coated with a light-sensitive composition having the following formula to form 2.5 g/m^2 of dry coating and then dried to form a light-sensitive layer.

Light-sensitive Composition

Ester compound of naphthoquinone-1,2-diazide-5-sulfonyl chloride and pyrogallol-acetone resin (disclosed in Example 1 of United States Patent No. 3,635,709)	0.75g
Cresol novolak resin	2.00g
OILBLUE #603 (available from ORIENT CHEMICAL INDUSTRY Co.,Ltd)	0.04g
Ethylene dichloride	16 g
2-Methoxyethyl acetate	12 g

The above prepared presensitized plate was imagewise exposed in a vaccum frame, through a positive transparency, to light from a 3 kW metal halide lamp at a distance of 1 m for 50 seconds. Then the exposed plate was developed with 3.50 % aqueous solution of sodium silicate (pH = 12.9) having a 0.83 molar ratio of SiO_2/Na_2O.

After being developed, the plate was fully washed with water, gummed up and subjected to printing in a usual manner. ① Strength of non-image areas, ② corrosion resistance of non-image areas, ③ dye stains on non-image areas, ④ reproduction of highlight areas, ⑤ hydrophilicity after development and ⑥ printing durability were estimated. The results are shown in Table 3.

The degree of dissolution of the anodized layer in the alkaline developer was graded according to the amount of scum remaining in the developer after 10 m^2 of the exposed plate per one liter of the developer was developed. The result was shown in Table 4.

Example 12

The procedures of Example 11 were repeated except that the substrate was sealed by spraying directly the substrate with vapor maintained at 100 °C for 30 seconds to form a substrate having a 85 % sealing ratio regarding the anodized layer on the right-side surface and a sealing ratio of 95 % regarding the anodized layer on the back-side surface. These sealing ratios were measured by QUANTASORB. The printing properties of the obtained lithographic plate are shown in Table 3.

The degree of dissolution of the anodized layer in the alkaline developer was graded according to the amount of scum remaining in the developer after 10 m^2 of the exposed plate per one liter of the developer was developed. The result was shown in Table 4.

Example 13

The procedures of Example 11 were repeated except that the substrate was sealed by spraying directly the substrate with vapor maintained at 90 °C for 10 seconds to form a substrate having a 60 % sealing ratio regarding the anodized layer on the right-side surface and a sealing ratio of 60 % regarding the anodized layer on the back-side surface. These sealing ratios were measured by QUANTASORB. The printing properties of the obtained lithographic plate are shown in Table 3.

The degree of dissolution of the anodized layer in the alkaline developer was graded according to the amount of scum remaining in the developer after 10 m^2 of the exposed plate per one liter of the developer was developed. The result was shown in Table 4.

Comparative Example 8

The procedures of Example 11 were repeated except that the sealing was not carried out. The printing properties of the obtained lithographic plate are shown in Table 3.

The degree of dissolution of the anodized layer in the alkaline developer was graded according to the amount of scum remaining in the developer after 10 m^2 of the exposed plate per one liter of the developer was developed. The result was shown in Table 4.

Printing properties shown in Tables 1, 2 and 3 were estimated in the following manners.

Strength of Non-Image Areas

Non-image areas in a lithographic plate which was developed and gummed up were scratched using a diamond needle with a load of from 100 to 400 g by a scratch test machine availble from Sinto Science Co., Ltd. Results were graded as follows:

A: No scratch was produced with a load of 200 g.
B: Scratches were produced with a load of 200 g but not with a load of 100 g.
C: Scratches were produced with a load of 100 g.

Corrosion Resistance of Non-image Areas

A lithographic plate was immersed in a commercially available plate cleaner and then non-image areas were rubbed 500 times with a rubber blanket in a printing machine. The degree of attrition in the non-image areas was graded as follows:

A: Attrition of the anodized layer was not observed.
B: Slight attrition of the anodized layer was observed.
C: The anodized layer was completely exhausted.

Dye Stains on Non-image Areas

The difference (Δ D) was measured between the reflective optical density of 600 nm light of the non-image areas in a lithographic plate after development, and that of the substrate surface before application of a light-sensitive layer. The difference obtained was graded as follows:

A: $\Delta D \leqq 0.005$
B: $0.005 < \Delta D \leqq 0.01$
C: $0.01 < \Delta D \leqq 0.02$

D: $0.02 < \Delta D \leqq 0.03$
E: $0.03 < \Delta D \leqq 0.04$
F: $0.04 < \Delta D$

Reproduction of Highlight Areas

A presensitized plate was exposed to light with a K value chart of FOGRA under constant conditions, developed and gummed up. The resulting lithographic plate was subjected to printing and the reproduction of highlight areas was graded in the following standard based on the K value of the minimun width line reproduced in the prints.

A: K value ≦ 10 μ
B: 12 μ ≦ K value ≦ 15 μ
C: 20 μ ≦ K value

Hydrophilicity after Development

The contact angle of a droplet of water in oil on non-image areas after development was measured. The hydrophilicity of the non-image areas was graded as follows:

A: below 10 °
B: from 20 to 40 ° C: above 60 °

Staining of Non-image Areas

A presensitized plate was preserved at 45 °C and 75 % relative humidity for 3 days and then made into a lithographic plate. The lithographic plate was subjected to printing and the degree of staining of the non-image areas was graded as follows:

A: No staining was observed.
B: A slight amount of staining was observed.
C: A large amount of staining was observed.

Reproduction of Halftone Dots in Shadow Areas

A presensitized plate was exposed to light with a K value chart of FOGRA under constant conditions, developed and gummed up. The resulting lithographic plate was subjected to printing and the reproduction of halftone dots in shadow areas was graded in the following standard based on the K value of the minimum width reproduced in the prints.

A: K value ≦ 10 μ
B: 12 μ ≦ K value ≦ 15 μ
C: 20 μ ≦ K value

Printing durabilities in Table 1 are shown as relative values with the printing durability of the lithography plate prepared in Example 1 being made equal to 100 %.

Printing durabilities in Table 2 are shown as relative values with the printing durability of the lithography plate prepared in Example 7 being made equal to 100 %.

Printing durabilities in Table 3 are shown as relative values with the printing durability of the lithography plate prepared in Example 11 being made equal to 100 %.

Amounts of scum in the developer in Table 4 are graded as follows:

A: No scum was produced.
B: A little amount of scum was produced.
C: A large amount of scum was produced.

While the present invention has been illustrated by means of several preferred embodiments, one of ordinary skill in the art will recognize that modifications and improvements can be made while remaining within the scope of the invention. The scope of the invention is determined solely by the appended claims.

Table 1 Printing Properties

	Example						Comparative Example			
	1	2	3	4	5	6	1	2	3	4
Anodized Layer (g/m²)	4.0	2.0	5.0	4.0	6.0	4.0	4.0	1.0	4.0	4.0
Sealing Ratio (%)	60	40	95	60	60	60	60	60	0	100
Undercoating or Hydrophilizing Treatment	(a)	(a)	(a)	(b)	(a)	(b)	–	(a)	(a)	(a)
① Strength of Non-image Areas	A	A	A	A	A	A	A	B	A	A
② Corrosion Resistance of Non-image Areas	A	A	A	A	A	A	A	A	B	A
③ Dye Stains on Non-image Areas	B	B	B	B	D	B	F	A	F	A
④ Reproducibility of Highlight Areas	B	B	B	B	B	B	B	B	C	B
⑤ Hydrophilicity after Development	B	B	B	B	B	B	B	C	A	C
⑥ Printing Durability (%)	100	100	100	100	100	100	100	100	100	80

(a): β-Alanine Undercoating (b): Polyviny Phosphonic Acid Treatment

Table 2 Printing Properties

	Example 7	Example 8	Example 9	Example 10	Comparative Example 5	Comparative Example 6	Comparative Example 7
Anodized Layer (g/m^2)	4.0	2.0	5.0	6.0	1.0	4.0	4.0
Sealing Ratio (%)	60	40	95	60	60	0	100
① Strength of Non-image Areas	A	A	A	A	B	A	A
② Staining of Non-image Areas	A~B	A~B	A~B	B	A	C	C
③ Reproduction of Halftone Dots in Shadow Areas	B	B	B	B	B	C	B
④ Hydrophilicity of Non-image Areas	B	B	B	B	C	A	C
⑤ Printing Durability (%)	100	100	100	100	100	100	80

Table 3 Printing Properties

		Example			Comparative Example
		11	12	13	8
Anodized Layer (g/m²)	*R	2.5	2.5	2.5	2.5
	B	0.5	0.5	0.5	0.5
Sealing Ratio (%)	R	85	85	60	0
	B	95	95	60	0
Undercoating or Hydrophilizing Treatment		β-Alanine Undercoating	β-Alanine Undercoating	β-Alanine Undercoating	β-Alanine Undercoating
① Strength of Non-image Areas		A	A	A	A
② Corrosion Resistance of Non-image Areas		A	A	A	B
③ Dye Stains on Non-image Areas		B	B	B	F
④ Reproducibility of Highlight Areas		B	B	B	C
⑤ Hydrophilicity after Development		B	B	B	A
⑥ Printing Durability (%)		100	100	100	100

*R and B mean the right-side surface and the back-side surface of the aluminum plate, respectively.

Table 4 Amount of Scum in the Developer

		Example			Comparative Example
		1 1	1 2	1 3	8
Sealing System		Boiling System at 100℃ for 30 seconds	Vapor Spraying System at 100℃ for 30 seconds	Vapor Spraying System at 90 ℃ for 10 seconds	—
Sealing Ratio (%)	*R	85	85	60	0
	B	95	95	60	0
Amount of Scum in the Developer		A	A	B	C

* R and B mean the right-side surface and the back-side surface of the aluminum plate, respectively.

Claims

1. A process for preparing a substrate for a lithographic plate, which comprises the steps of subjecting at least one surface of an aluminum plate to a surface roughening treatment, anodizing the resulting plate to form at least 2 g/m^2 of an anodized layer, sealing the anodized plate with hot water or water vapor to reduce the surface area of the anodized layer by from 40 to 95 % and subjecting the sealed plate to at least one of a hydrophilizing treatment or a hydrophilic-undercoating treatment.

2. The process according to Claim 1, wherein the step of sealing is carried out with water vapor.

3. The process according to Claim 1, wherein the aluminum plate is subjected to a roughening treatment to have a surface roughness of from 0.3 to 1.0μ.

4. The process according to Claim 1, wherein the amount of the anodized layer is from 2 to 5 g/m^2.

5. The process according to Claim 1, wherein the anodized plate was sealed to reduce the surface area of the anodized layer by from 60 to 90 %.

6. The process according to Claim 1, wherein the hydrophilizing treatment is carried out by treating the sealed plate with polyvinyl phosphonic acid.

7. The process according to Claim 1, wherein the hydrophilizing treatment is carried out by treating the sealed plate with sodium silicate.

8. The process according to Claim 1, wherein the hydrophilic-undercoating treatment is carried out by undercoating the sealed plate with β -alanine.

9. A process of preparing a presensitized lithographic printing plate precursor which comprises the steps of subjecting at least one surface of an aluminum plate to a surface-roughening treatment; anodizing to form at least 2 g/m^2 of an anodized layer; sealing the anodized layer with hot water or water vapor to reduce the surface area of the anodized layer by from 40 to 95 %; at least one of hydrophilizing treatmant or applying a hydrophilic-undercoating;and coating a lithographically suitable light-sensitive layer, in said order.

10. The process according to Claim 9, wherein the step of sealing is carried out with water vapor.

11. The process according to Claim 9, wherein the light-sensitive layer comprises an o-quinonediazide compound.

12. The process according to Claim 9, wherein the light-sensitive layer comprises a diazide resin and a binder.

13. The process according to Claim 9, wherein said steps are subjected to one surface of the aluminum plate and the other surface of the aluminum plate is subjected to anodizing to form an anodized layer in an range of from 0.05 to 1.0 g/m^2 followed by sealing with hot water or water vapor to reduce the surface area of the anodized layer at the other side of the aluminum plate by at least 80 %.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9284

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.5)
Y	DE-A-3 717 757 (FUJI PHOTO FILM CO., LTD.) * example 1 *	1-13	B41N3/03 C25D11/18
Y,D	PATENT ABSTRACTS OF JAPAN vol. 8, no. 234 (M-334)(1671) 26 October 1984 & JP-A-59 114 100 (FUJI SHASHIN FILM K.K.) 30 June 1984 * abstract *	1-13	
Y	US-A-4 284 674 (H.W.LEYH) * figures 1,2 * * column 4, line 67 - column 5, line 13 *	13	
A	US-A-4 116 695 (T.MORI ET AL) * column 5, line 12 - column 6, line 29 * * examples *	1	
A	EP-A-0 149 490 (FUJI PHOTO FILM CO., LTD.) * abstract *	1	
D	& JP-A-60 149 491 (...)		
A	US-A-3 468 725 (F.UHLIG) * the whole document *	1	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	US-A-4 390 407 (T.MORI ET AL) * abstract * * example 1 *	13	B41N C25D
D	& DE-A-3 135 747		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 FEBRUARY 1992	MARKHAM R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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