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(54) **Method for producing substrate for PS plate.**

(57) A method for producing a substrate for a presensitized plate for use in making a lithographic printing plate comprises surface-roughening and anodizing an aluminum plate, wherein the surface-roughened and anodized aluminum plate is then, in order, subjected to the following treatments:

- (a) a dyeing treatment with a dye;
- (b) a sealing treatment; and
- (c) an optional hydrophilization treatment. The method can provide an excellent aluminum substrate for presensitized plates which are excellent in half tone dot reproduction, resistance to background contamination, ability of recovering from contamination with ink and easy achievement of good balance between water and ink and which can correspondingly provide lithographic printing plate having high printing durability.

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METHOD FOR PRODUCING SUBSTRATE FOR PS PLATE

BACKGROUND OF THE INVENTION

The present invention relates to a method for producing a substrate for a presensitized plate for use in making a lithographic printing plate (hereinafter referred to as "PS plate" and in particular to a method for producing an aluminum plate having a roughened surface for PS plates.

A so-called PS plate which comprises an aluminum substrate provided thereon with a thin layer of a light-sensitive composition is in general produced by subjecting an aluminum plate to a surface roughening treatment by, for instance, a mechanical method such as brush graining or ball graining, an electrochemical method such as electrolytic graining or a combination thereof to form a grained surface; etching the surface with an aqueous solution of an alkali or acid; further anodizing the aluminum plate; optionally hydrophilizing the surface thereof; and applying a light-sensitive layer to the surface.

The PS plate thus produced is generally exposed to light, developed, image-corrected and then gummed-up to give a lithographic printing plate which is set on a printing press to form printed matters.

However, image areas obtained by imagewise exposing, to light, a positive-working PS plate which comprises a conventional substrate for PS plate provided thereon with a positive-working light-sensitive layer are formed from half tone dots having a size smaller than that for those on an original and hence the reproduction of highlight portions is insufficient. On the other hand, image areas obtained by imagewise exposing, to light, a negative-working PS plate which comprises a conventional substrate for PS plate provided thereon with a negative-working light-sensitive layer are formed from half tone dots having a size greater than that for those on an original and hence the half tone dots on shadowed portions are liable to be filled-in.

Many attempts have been directed to solve these problems, for instance, Japanese Patent Unexamined Publication (hereunder referred to as "J.P. KOKAI") No. Sho 61-122649 proposes a method in which a positive-working light-sensitive layer is applied onto an anodized aluminum substrate after applying an underlying layer of a halation-inhibiting dye thereto.

In addition, U.K. Patent No. 1,069,283 discloses a method which comprises anodizing an aluminum substrate, applying an underlying layer of a bichromate, an alkali metal silicate or a dye and then applying a light-sensitive layer. U.S. Patent No. 4,217,555 proposes a method comprising anodizing a substrate, then hydrophilizing it to charge it negative and ionically dyeing with a cationic dye.

J.P. KOKAI No. Sho 60-64352 proposes a method which comprises surface-roughening and hydrophilizing an aluminum plate and then dyeing it with a monobasic acid type acidic dye.

J.P. KOKAI No. Sho 58-14797 discloses a method comprising the steps of surface-roughening an aluminum plate, etching it with an alkali and then forming a colored anodized layer thereon.

The substrates thus prepared suffer from problems that the dyes applied onto the surface are liable to migrate into light-sensitive layers ultimately applied thereto and, therefore, the function of the coated dye as a halation-inhibiting layer is impaired. For this reason, a large amount of dye should be employed to improve the half tone dot reproduction. However, in this case, the dye used remains unremoved on non-image areas which leads to the occurrence of background contamination.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a method for producing a substrate for use in making a PS plate which is excellent in various properties such as reproduction of half tone dots, resistance to background contamination (on non-image areas), ability of recovering from contamination with ink and easy achievement of good balance between water and ink.

Another object of the present invention is to provide a method for producing a substrate favorable for making a PS plate which can provide a lithographic printing plate having high printing durability.

A further object of the present invention is to provide a method for producing an aluminum plate having a roughened surface favorable for use in making PS plates.

The foregoing objects of the present invention can effectively be attained by providing a method for producing an aluminum substrate for PS plate which comprises surface-roughening and anodizing an aluminum plate and then subjecting it to the following treatments in order:

- (a) a coloring treatment with a dye;
- (b) a sealing treatment; and

(c) an optional hydrophilization treatment.

DETAILED DESCRIPTION OF THE INVENTION

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The method of the present invention will hereunder be described in more detail.

(Aluminum Plate)

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The aluminum plate used in the present invention is, for instance, a plate-like material of pure aluminum, an aluminum alloy mainly comprising aluminum and trace amounts of other elements or the like. Examples of such elements other than aluminum include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of these elements are in general not more than 15 10% by weight. The substrate is preferably a pure aluminum plate in the present invention, but it is difficult to obtain completely pure aluminum in view of the present situation of refining techniques. For this reason, aluminum having contents of other elements as low as possible is preferably employed in the present invention. However, the composition of the aluminum plates used in the invention is not restricted to a specific one and the aluminum plate can arbitrarily be selected from any known and commonly used 20 materials such as JIS A1050, JIS A1100, JIS A1200, JIS A3103, JIS A3003 and JIS A5005. The thickness of the aluminum plate used in the invention preferably ranges from about 0.1 to 0.5 mm.

(Surface-Roughening Treatment)

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The surface of an aluminum plate is subjected to degreasing treatment with, for instance, a surfactant or an aqueous solution of an alkali to remove rolling oils present thereon and then surface-roughened prior to an anodization treatment.

The surface-roughening treatment can be carried out by a mechanical surface-roughening treatment, an 30 electrochemical surface-roughening treatment or a method for selectively dissolving the surface chemically. The mechanical surface-roughening treatment can be performed by any known methods such as ball graining, brush graining, sand blast graining and honing. The electrochemical surface-roughening treatment can be carried out by, for instance, passing an electric current (either DC or AC) through an aluminum plate in an electrolyte such as a hydrochloric acid or nitric acid solution. Moreover, a combination of a 35 mechanical and electrochemical surface-roughening treatments may also be employed as disclosed in J.P. KOKAI No. Sho 54-63902.

The aluminum plate thus surface-roughened is, if necessary, subjected to an alkali etching treatment and a neutralization treatment.

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(Anodization Treatment)

The surface of aluminum plates thus treated is subsequently anodized.

Any electrolytes capable of forming a porous oxidized layer may be used in the anodization treatment 45 of the aluminum plate and examples thereof commonly used are baths of sulfuric acid, phosphoric acid, oxalic acid, chromic acid or mixture thereof; or baths of sodium hydroxide, potassium hydroxide or mixture thereof; or baths to which ammonium fluoride is added. The concentration of these baths varies depending on the kinds of electrolytes to be added thereto. The conditions of the anodization greatly vary depending on the kinds of electrolytes used and cannot be restricted to specific ones, but in general those for the 50 anodization are the concentration of electrolyte ranging from 1 to 80% by weight, an electrolyte temperature ranging from 5 to 80 ° C, a current density ranging from 5 to 80 A/dm², an electric voltage ranging from 1 to 100 V, and an electrolysis time ranging from 5 seconds to 10 minutes.

Particularly preferred anodization is performed in sulfuric acid solution as an electrolyte in the present invention and preferably the anodization is carried out under the conditions as set forth in U.K. Patent No. 1,412,768 and U.S. Patent No. 4,211,619. 55

The most preferred anodization is performed in the electrolyte comprising from 5 to 20 % by weight of sulfuric acid and 3 to 15 % by weight of aluminum ions at a temperature of from 25 to 50 ° C at a mean current density of from 5 to 20 A/dm².

The amount of the anodized layer to be formed preferably ranges from 0.1 to 10 g/m² and more preferably 1 to 6 g/m².

5 (Dyeing Treatment)

The surface of the aluminum plate which has been anodized is then colored with a dye.

The term "dyeing treatment" herein means a treatment for dyeing the aluminum plate which has been anodized in a desired color with a dye and may be performed by, for instance, coating or spraying an aqueous solution of a dye on the aluminum plate; by dipping the aluminum plate in an aqueous solution of a dye; or dipping the aluminum plate in an aqueous solution of a dye and simultaneously electrolyzing. Any dyes may be used in the invention so far as they can dye the anodized layer on the aluminum plate, but in general acidic dyes, direct dyes or the like are employed.

The aqueous solution of a dye may optionally comprise additives capable of providing anodized layers uniformly dyed.

The conditions for the dyeing vary depending on the desired extent of dyeing and cannot be specified to particular conditions, but when the dyeing is performed by dipping treatment, the desirable conditions for dyeing are a dye concentration ranging from 0.1 to 10 g/l; a dyeing temperature ranging from 20 to 70 °C; and a processing time ranging from 2 seconds to 2 minutes.

The absorption wavelength region of the dyed aluminum plate must be superposed with the wavelengths to which the light-sensitive composition applied thereto is sensitive in order to ensure the halation-inhibiting effect. The term "wavelengths to which the light-sensitive composition is sensitive" means those falling within the absorption region of the light-sensitive composition which coincides with the wavelength of the light source for exposure. For instance, if a light-sensitive composition containing a diazo compound having an absorption ranging from 300 nm to 500 nm is exposed to light with a metal halide lamp having bright line spectra at 407 and 415 nm, the dyed layer must have an absorption at a wavelength of 407 or 415 nm. The degree of dyeing is controlled so that the increase in the optical density due to the dyeing ranges from 0.05 to 0.25 expressed in the optical density of reflected light. Of course, the value must be determined at a wavelength of 407 or 415 nm when the resulting PS plate is exposed to light from the foregoing metal halide lamp.

Specific examples of dyes having an absorption within this wavelength region include Alumat Yellow 3GL and Basalox Yellow GLN (C.I. Acid Yellow 176) (both available from Kaname Shokai), Aluminium Yellow G3LW (C.I. Acid Yellow 167) (available from Sandoz A.G.), Kayafect Yellow A (available from Nippon Kayaku), C.I. Acid Yellow 23 (Tertradine), C.I. Acid Yellow 25, C.I. Acid Yellow 36, C.I. Acid Yellow 38, C.I. Acid Orange 10, C.I. Acid Red 13, C.I. Direct Yellow 8, C.I. Direct Yellow 12 and C.I. Direct Yellow 27.

However, these dyes have yellow or orange color and if the aluminum plate is dyed with these dyes, the resulting non-image areas are also colored yellow, which impairs the plate examination properties. To prevent the occurrence of this phenomenon, the aluminum plate must be dyed with a gray or black dye or with a mixed dye comprising yellow, red, blue dyes or the like. Thus, gray colored non-image areas can be obtained and the deterioration of the plate examination properties can be prevented while maintaining the ability of absorbing light of the foregoing wavelength. Specific examples of gray and black dyes are Aluminium Gray NL and Aluminium Black 2LW (both available from Sandoz A.G.) and Basalox Black WL (available from Kaname Shokai). Mixed dyes for obtaining a gray surface are, for instance, Sanodal Deep Black MLW (available from Sandoz A.G.) or the like. Alternatively, it is also possible to use any arbitrary mixture of commercially available red, blue, yellow dyes or the like.

(Sealing Treatment)

The surface of the aluminum plate which has been dyed with a dye is then subjected to a sealing treatment.

The term "sealing treatment" herein means a processing which comprises exposing, to water vapor atmosphere, an aluminum plate provided with a porous anodized layer thereon, or dipping it in hot water or electrolyzing it in an electrolyte to thus seal pores of the porous anodized layer with a metal, an oxide or a hydroxide.

If the sealing treatment is performed with steam (viz., aqueous vapor), there may be employed steam under pressure or under normal pressure. If it is carried out in hot water, the hot water may comprise a variety of additives having an effect of accelerating the sealing treatment. If the aluminum plate is sealed by

electrolyzing in an electrolyte, examples of the electrolytes used are those containing various kinds of oxo acids or salts thereof or inorganic fine particles. The methods for sealing treatment are not restricted to these specific ones and any methods capable of sealing pores of a porous film may be employed.

Among these sealing methods, preferred is the method for sealing with water vapor. In this case, steam
5 under pressure or under normal pressure may be used as described above.

The sealing treatment in which steam is used can preferably be performed at a relative humidity of not less than 70%, a steam temperature of not less than 95 °C for 2 seconds to 2 minutes.

This sealing treatment makes it possible to prevent the migration of the dye from the anodized layer to the light-sensitive layer subsequently applied during application of the light-sensitive layer and/or develop-
10 ment of the resulting PS plate. Moreover, the sealing treatment makes it possible to solve the problem that the components of the light-sensitive layer such as dyes and/or polymer binders adsorb on the surface of the substrate irreversibly with the lapse of time to thus cause contamination. The PS plate obtained by applying a light-sensitive layer onto the substrate thus obtained has excellent storage stability (shelf life).

The aluminum plate which has thus been sealed can be immediately used as a substrate for PS plate
15 as such. For instance, it may be used as a substrate for wipe-on lithographic plate or used for making a PS plate by applying a light-sensitive layer suitable for lithographic printing. However, the aluminum plate may further be subjected to a hydrophilization treatment, an application of a hydrophilic underlying coating or combination thereof, after the sealing treatment.

20

(Hydrophilization Treatment)

In the present invention, the hydrophilization treatment can be performed by any known method such as treatment with an alkali metal silicate (e.g., an aqueous solution of sodium silicate) as disclosed in U.S.
25 Patent Nos. 2,714,066 and 3,181,461; with potassium fluorozirconate as disclosed in Japanese Patent Publication for Opposition Purpose (hereunder referred to as "J.P. KOKOKU") No. 36-22063; or with a polyvinylsulfonic acid as disclosed in U.S. Patent Nos. 4,153,461 and 4,689,272. If the light-sensitive layer comprising a diazo resin is applied onto the aluminum substrate, the aluminum substrate is preferably subjected to such a hydrophilization treatment.

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(Hydrophilic Underlying Coating Layer)

Preferred examples of the hydrophilic underlying coatings are those disclosed in J.P. KOKAI Nos. Sho
35 60-149491, Sho 60-232998 (EP-B-149490), Sho 62-19494 and Sho 59-101651 (EP-A-110417). This underlying coating may be applied after the foregoing sealing treatment or after the sealing treatment and the foregoing hydrophilization treatment.

Unexpectedly, the substrate of the present invention has excellent tone reproduction and resistance to contamination with ink during printing since the substrate which has been anodized, dyed with a dye and
40 then sealed as detailed above has halation inhibiting effect higher than that for the substrate obtained by a conventional method.

The substrate obtained by the method of this invention may be used in making a PS plate by applying a light-sensitive layer as will be detailed below to the surface thereof.

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(I) Light-Sensitive Layer Comprising Diazo Resin and Binder

As negative-working light-sensitive diazo compounds, preferably used are, for instance, condensed products of formaldehyde with diphenylamine-p-diazonium salt which is a reaction product of a diazonium
50 salt with an organic condensing agent having a reactive carbonyl group such as aldol or acetal (so-called light-sensitive diazo resins) as disclosed in U.S. Patent Nos. 2,063,631 and 2,667,415. In addition to the foregoing compounds, useful examples of condensed diazo compounds further include those disclosed in J.P. KOKOKU Nos. Sho 49-48001, Sho 49-45322 and Sho 49-45323. The light-sensitive diazo compounds of this type can usually be obtained in the form of water-soluble inorganic salts and, therefore, these
55 compounds can be applied in the form of an aqueous solution to form a light-sensitive layer. Alternatively, it is also possible to use substantially water-insoluble light-sensitive diazo resins which are reaction products of the foregoing water-soluble diazo resins with aromatic or aliphatic compounds having either or both of at least one phenolic hydroxyl group and a sulfonic acid residue by the method as disclosed in J.P. KOKOKU

No. Sho 47-1167 (US.Pat. No. 3,300,309).

Moreover, the diazo resins may also be used as a reaction product with a hexafluorophosphate or tetrafluoroborate as disclosed in J.P. KOKAI No. Sho 56-121031.

Examples of the reaction products carrying a phenolic hydroxyl group are diphenolic acids such as hydroxybenzophenone, 4,4-bis(4'-hydroxyphenyl)pentanoic acid, resorcinol and diresorcinol, which may have other substituents. Hydroxybenzophenones include, for instance, 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone. Preferred examples of the sulfonic acids are aromatic sulfonic acids such as benzenesulfonic acid, toluenesulfonic acid, xylenesulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, naphthol-sulfonic acid and benzophenonesulfonic acid; or soluble salts thereof such as ammonium and alkali metal salts. The compounds carrying a sulfonic acid residue may in general be substituted with lower alkyl groups, nitro groups, halogen atoms and/or another sulfonic acid residue. Preferred examples of such compounds are benzenesulfonic acid, toluenesulfonic acid, naphthalenesulfonic acid, 2,5-dimethylbenzenesulfonic acid, sodium benzenesulfonate, 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)benzenesulfonate, alizarinsulfonic acid, o-toluidine-m-sulfonic acid and ethanesulfonic acid. Useful examples thereof also include sulfuric acid esters of alcohols or aromatic hydroxy compounds or salts thereof. Such compounds may usually easily be available as anionic surfactants. Examples thereof are ammonium or alkali metal salts of lauryl sulfate, alkylaryl sulfate, p-nonylphenyl sulfate, 2-phenylethyl sulfate and isooctylphenoxy diethoxyethyl sulfate.

These substantially water-insoluble light-sensitive diazo resins are isolated as precipitates by mixing water-soluble light-sensitive diazo resins with an aqueous solution of the foregoing aromatic or aliphatic compounds in an approximately equivalent amount.

In addition, diazo resins disclosed in U.K. Patent No. 1,312,925 are also preferably used in the invention.

The most preferred diazo resin is 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonic acid salt or hexafluorophosphate of a condensate of p-diazodiphenylamine and formaldehyde.

The light-sensitive layer preferably comprises the diazo resin in an amount ranging from 5 to 50% by weight. If the amount of the diazo resin is decreased, the sensitivity to light of the resulting light-sensitive layer is correspondingly increased, but the stability with the lapse of time is lowered. Therefore, the most preferred amount of the diazo resin ranges from about 8 to 20% by weight.

On the other hand, a variety of polymeric compounds may be used as binders. Examples thereof preferably used in the invention are those carrying hydroxyl, amino, carboxyl, amido, sulfonamido, active methylene, thioalcohol, epoxy groups or the like. Specific examples thereof are shellac disclosed in U.K. Patent No. 1,350,521; polymers comprising, as main repeating units, hydroxyethyl acrylate units or hydroxyethyl methacrylate units as disclosed in U.K. Patent No. 1,460,978 and U.S. Patent No. 4,123,276; polyamide resins disclosed in U.S. Patent No. 3,751,257; phenol resins and polyvinyl acetal resins such as polyvinyl formal resins and polyvinyl butyral resins disclosed in U.K. Patent No. 1,074,392 and U.S. Pat. Nos. 4,631,245 and 4,741,985; linear polyurethane resins disclosed in U.S. Patent Nos. 3,660,097 and 4,877,711 and U.K. Pat. No. 2,185,120; phthalate derivatives of polyvinyl alcohol resins, epoxy resins obtained by condensing bisphenol A with epichlorohydrin, amino group-containing resins such as polyaminostyrene and polyalkylamino(meth)acrylate, and cellulose derivatives such as cellulose acetate, cellulose alkyl ether and cellulose acetate phthalate.

The composition comprising a diazo resin and a binder may further comprise additives such as a pH indicator as disclosed in U.K. Patent No. 1,041,463 and phosphoric acid and a dye as disclosed in U.S. Patent No. 3,236,646.

(II) Light-Sensitive Layer Comprising o-Quinonediazide Compound

Particularly preferred o-quinonediazide compounds are o-naphthoquinonediazide compounds and examples thereof are described in a variety of publications such as U.S. Patent Nos. 2,766,118; 2,767,092; 2,772,972; 2,859,112; 2,907,665; 3,046,110; 3,046,111; 3,046,115; 3,046,118; 3,046,119; 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,061,430; 3,102,809; 3,106,465; 3,635,709; and 3,647,443, which can be suitably used in the invention. Among these, preferred are o-naphthoquinonediazidesulfonic acid esters or o-naphthoquinonediazide-carboxylic acid esters of aromatic hydroxyl compounds and o-naphthoquinonediazidesulfonic acid amides or o-naphthoquinonediazide carboxylic acid amides of aromatic amino compounds and particularly preferred are condensates of pyrogallol and acetone which is esterified

with o-naphthoquinonediazidesulfonic acid as disclosed in U.S. Patent No. 3,635,709; polyesters carrying a hydroxyl group at the end thereof which is esterified with o-naphthoquinonediazidesulfonic acid or o-naphthoquinonediazidecarboxylic acid as disclosed in U.S. Patent No. 4,028,111; homopolymers of p-hydroxystyrene or copolymer of the monomer with other copolymerizable monomers, which is esterified
 5 with o-naphthoquinonediazidesulfonic acid or o-naphthoquinonediazidecarboxylic acid as disclosed in U.K. Patent No. 1,494,043; homopolymers of p-aminostyrene or copolymers of the monomer with other copolymerizable monomers, which are reacted with o-naphthoquinonediazidesulfonic acid or o-naphthoquinonediazidecarboxylic acid to form amides thereof as disclosed in U.S. Patent No. 3,759,711.

These o-quinonediazide compounds may be used singly, but preferably they are used in combination
 10 with an alkali-soluble resin. The alkali-soluble resins are preferably novolak type phenol resins and specific examples thereof are phenol/formaldehyde resins, o-cresol/formaldehyde resins and m-cresol/formaldehyde resins. More preferably, the foregoing phenol resin is used together with a condensate of phenol or cresol substituted with an alkyl group having 3 to 8 carbon atoms with formaldehyde such as t-butylphenol/formaldehyde resin as disclosed in U.S. Patent No. 4,123,279. The composition for forming a
 15 light-sensitive layer may comprise such an alkali-soluble resin in an amount ranging from about 50 to about 85% by weight and preferably 60 to 80% by weight on the basis of the total weight of the composition.

Furthermore, a polymer having a sulfonamide group in the molecule as described in EP-A-330239 can be used as an alkali-soluble resin.

The light-sensitive composition comprising o-quinonediazide compound may further comprise, if necessary, other additives such as a dye, a plasticizer and/or a component for imparting printing out properties to the light-sensitive layer such as those disclosed in U.K. Patent Nos. 1,401,463 and 1,039,475 and U.S. Patent No. 3,969,118. (III) Light-Sensitive Layer (obtained from a photopolymerizable light-sensitive composition comprising a polymer carrying carboxylic acid residues or anhydrous carboxylic acid residues, an addition polymerizable unsaturated compound and a photopolymerization initiator):

25 If a photopolymerizable light-sensitive materials are employed, the surface of a substrate which has been grained in a hydrochloric acid bath is preferably anodized in phosphoric acid or a mixed acid of phosphoric acid and sulfuric acid.

A layer of a photopolymerizable light-sensitive composition comprising a polymer carrying carboxylic acid residues or carboxylic acid anhydride residues, an addition polymerizable unsaturated compound and
 30 a photopolymerization initiator is applied onto the surface of a substrate which has been anodized in a phosphoric acid bath and then treated with a silicate. The lithographic printing plate obtained from the PS plate thus prepared is excellent in storability and the exposed surface of the aluminum substrate on non-image areas is hardly contaminated with a printing ink and has good hydrophilicity which makes it possible to rapidly remove the adhered ink and the aluminum surface has high adhesion to the light-sensitive layer.

35 As the polymer carrying carboxylic acid residues or carboxylic acid anhydride residues favorable for this purpose, preferred are those comprising structural units selected from the group consisting of those represented by the following general formulae (A) to (D):

(A)

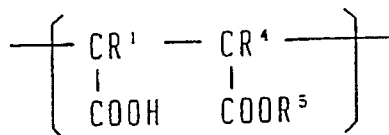
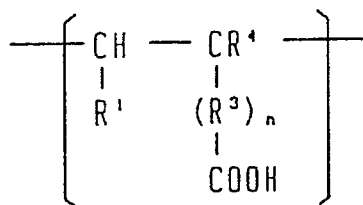
(B)

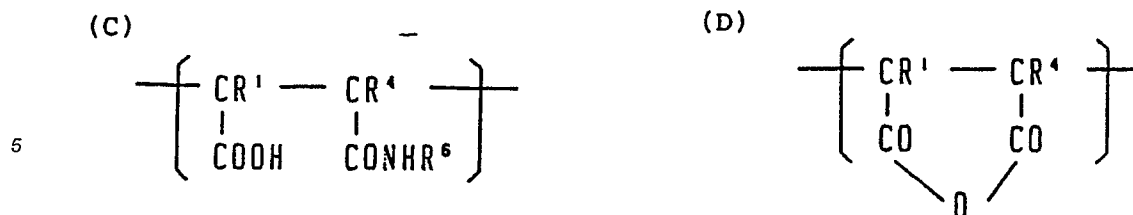
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wherein R¹ and R⁴ each represents a hydrogen, atom or an alkyl group; R³ represents a phenylene group or an alkylene group which may have a hydroxyl group; R⁵ represents a hydrogen atom or a substituted or unsubstituted alkyl group; R⁶ represents a substituted or unsubstituted alkyl, aryl or allyl group or a cycloalkyl group; and n is 0 or 1. More specifically, examples of units (A) are those derived from acrylic acid, methacrylic acid, crotonic acid and vinyl benzoate; examples of units (B) are those derived from maleic acid, monohydroxyalkyl maleate and monocyclohexyl maleate; examples of units (C) are those derived from maleic acid monoalkylamide and maleic acid monohydroxyalkylamide; and examples of units (D) are those derived from maleic anhydride and itaconic anhydride. In the invention, polymers having an average molecular weight ranging from 1,000 to 100,000 are in general employed.

The addition polymerizable unsaturated compounds are monomers having an ethylenically unsaturated double bond which causes three-dimensional addition polymerization when the photopolymerizable light-sensitive composition is irradiated with actinic light rays to thus form an insoluble product. Specific examples thereof are unsaturated carboxylic acids, esters of unsaturated carboxylic acids and aliphatic polyhydroxy compounds and esters of unsaturated carboxylic acids and aromatic polyhydroxy compounds.

Examples of the photopolymerization initiators are benzoin, benzoin alkyl ether, benzophenone, anthraquinone and Michler's ketones which may be used alone or in combination.

The light-sensitive composition of this type is preferably applied onto the surface of the substrate in an amount ranging from 1 to 3 g/m² (weighed after drying).

(IV) Light-Sensitive Layer for Electrophotography

An electrophotographic light-sensitive layer principally comprises a photoconductive compound and a binder, but may further comprise a known pigment, a dye, a chemical sensitizer and/or other additives for improving the sensitivity, for imparting a desired wavelength region to which the compound is sensitive to the electrophotographic light-sensitive layer. In this case, the light-sensitive layer may comprise a single layer or a multi-layered structure in which separate layers have the function of generating charges and that of transporting the charges respectively. A lithographic printing plate can be obtained by forming toner images on the light-sensitive layer and decoating the non-image areas while using the toner images as a resist layer according to a known electrophotographic process.

The light-sensitive compositions for electrophotography are, for instance, disclosed in a variety of publications such as 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, which can be suitably used in the invention.

The thickness of the light-sensitive layer in general ranges from 0.1 to 30 μm and preferably 0.5 to 10 μm.

In general, the foregoing light-sensitive composition is dissolved in water, an organic solvent or mixture thereof, the resulting solution is applied onto the substrate of the invention and then dried to obtain a PS plate.

The PS plate thus obtained is imagewise exposed to light from a light source containing actinic rays such as carbon arc lamp, a xenon lamp, a mercury lamp, a tungsten lamp or a metal halide lamp and then developed to give a lithographic printing plate.

The lithographic printing plate obtained by imagewise exposing, to light, a PS plate whose substrate is obtained according to the method of this invention and then developing the exposed plate has various excellent properties irrespective of the type of the PS plates (positive- or negative-working type one). For instance, it has excellent tone reproduction and no contamination of the non-image areas. It is easy to distinguish the image areas from non-image areas during the retouching process. No trace of retouching remains and correspondingly contamination of printed matters due to the presence of such traces of retouching is not caused. Further, it is excellent in resistance to scratches of the non-image areas and wear

resistance. Moreover, it has high printing durability. Besides, it is excellent in the ability of recovering from contamination with ink. In addition, since no light-sensitive layer remains after development, it is easy to achieve good balance between water and ink.

The method of the present invention will hereinafter be explained in more detail with reference to the following non-limitative working Examples and the effects practically attained by the present invention will also be discussed in detail in comparison with the following Comparative Examples. In the following Examples and Comparative Examples, the term "%" means "% by weight" unless otherwise specified.

Examples 1 to 3

The surface of an aluminum plate of JIS A1050 was grained with a rotary nylon brush and an aqueous suspension of pumice stone as an abrasive. The surface roughness (central line average surface roughness) of the aluminum plate at this stage was 0.5μ . After washing with water, the aluminum plate was immersed in a 10% aqueous solution of sodium hydroxide maintained at 70°C to perform etching so that the amount of aluminum dissolved was equal to 6 g/m^2 . The aluminum plate was washed with water, immersed in a 30% aqueous solution of nitric acid for one minute to neutralize and then washed with water sufficiently. Thereafter, the aluminum plate was electrolytically surface-roughened in a 0.7% aqueous solution of nitric acid for 20 seconds using a rectangular alternating waved voltage having an anode time voltage of 13 V and a cathode time voltage of 6 V (power source wave form as disclosed in J.P. KOKAI No. Sho 53-77702), then immersed in a 20% aqueous solution of sulfuric acid maintained at 50°C to clean the surface thereof and washed with water.

Furthermore, the aluminum plate was subjected to a porous anodized layer-forming treatment in a 20% aqueous solution of sulfuric acid using a direct current. The aluminum plate was electrolyzed at a current density of 2 A/dm^2 while adjusting the electrolyzing time so that an anodized layer is formed on a substrate in an amount of 4.0 g/m^2 .

Then the anodized aluminum plate was immersed in a 0.1% aqueous solution of Tertradine (C.I. Acid Yellow 23) having an absorption peak at 400 nm maintained at 30°C and then washed with water. In this dyeing process, the immersing time was changed to obtain three kinds of substrates dyed in different extents.

These substrates were treated in a chamber saturated with water vapor at 100°C , 1 atm. for 30 seconds to give substrates. These substrates had pale yellow color tone.

Thereafter, the substrates were immersed in a 2.5% aqueous solution of No. 3 sodium silicate maintained at 70°C for 30 seconds, washed with water and then the extent of the dyeing of each substrate was determined. A light-sensitive solution having the following composition was applied onto the substrates thus obtained and then dried to form a light-sensitive layer thereon. The coated amount of the light-sensitive layer was 2.0 g/m^2 (weighed after drying).

Component	Amount (g)
N-(4-hydroxyphenyl)methacrylamide/2-hydroxyethyl methacrylate/acrylonitrile/methyl methacrylate/methacrylic acid copolymer (molar ratio = 15:10:30:38:7; average molecular weight = 60,000)	5.0
PF ₆ salt of condensate of 4-diazodiphenylamine and formaldehyde	0.5
phosphorous acid	0.05
Victoria Pure Blue BOH (available from HODOGAYA CHEMICAL CO., LTD.)	0.1
2-methoxyethanol	100

The PS plates thus prepared were exposed to light from a 3 KW metal halide lamp for 50 seconds at a distance of 1 m, through a Fuji Film Step Guide and a K-value Film available from FOGRA CO., LTD. using a vacuum printing frame, then developed with a developer having the following composition, gummed-up with an aqueous solution of gum arabic to thus give lithographic printing plates.

Developer Composition:	
Component	Amount (g)
sodium sulfite	5
benzyl alcohol	30
sodium carbonate	5
sodium isopropyl naphthalenesulfonate	12
pure water	1000

The background contamination (or contamination of the non-image areas) and half tone dot reproduction of the resulting lithographic printing plates were examined. The results obtained are listed in the following Table I.

Examples 4 to 6

A substrate was produced in the same manner used in Examples 1 to 3 except that the dyeing treatment with a dye was performed using a 0.1% aqueous solution of Aluminium Yellow G3LW (available from Sandoz A.G.; in Ex. 4), Basalox Yellow GLN (available from Kaname Shokai; in Ex. 5) or Aluminium Gray NL (available from Sandoz A.G.; in Ex. 6) maintained at 30 ° C.

The color tone of the substrate of Example 6 which had been dyed with Aluminium Gray NL was gray stronger than that of the substrate observed before dyeing.

Subsequently, the extent of dyeing was determined and the substrate was subjected to a silicate treatment followed by application of a light-sensitive layer, exposure to light, a developing treatment and gumming-up treatment to thus give a lithographic printing plate as in the same manner used in Examples 1 to 3.

The contamination of the non-image areas and half tone dot reproduction of the resulting lithographic printing plate were determined. The results obtained are listed in the following Table I.

Comparative Examples 1 to 3

Substrates were prepared in the same manner used in Examples 1 to 3 except that the dyeing treatment with a dye or the sealing treatment was omitted, the extent of dyeing was determined and then the substrate was subjected to a silicate treatment followed by application of a light-sensitive layer, exposure to light, a developing treatment and gumming-up treatment to thus give a lithographic printing plate as in the same manner used in Examples 1 to 3.

The contamination of the non-image areas and half tone dot reproduction of the resulting lithographic printing plate were determined. The results obtained are listed in the following Table I.

Comparative Example 4

An aluminum plate was treated in the same manner used in Examples 1 to 3 till the anodization treatment and then immersed in a 2.5% aqueous solution of sodium silicate at 70 ° C for 30 seconds to form a substrate. Subsequently, a 1% aqueous solution of a cationic dye (C.I. BY-14) was applied to the substrate and dried. The extent of dyeing of the resulting substrate was determined. Then the substrate was subjected to a silicate treatment followed by application of a light-sensitive layer, exposure to light, a developing treatment and gumming-up treatment to thus give a lithographic printing plate as in the same manner used in Examples 1 to 3.

The contamination of the non-image areas and half tone dot reproduction of the resulting lithographic printing plate were determined. The results obtained are listed in the following Table I.

Comparative Example 5

An aluminum plate was treated in the same manner used in Examples 1 to 3 till the dyeing treatment with a dye and the extent of dyeing thereof was determined. Then the substrate was subjected to a silicate treatment followed by application of a light-sensitive layer, exposure to light, a developing treatment and gumming-up treatment to thus give a lithographic printing plate as in the same manner used in Examples 1 to 3. The contamination of the non-image areas and half tone dot reproduction of the resulting lithographic printing plate were determined. The results obtained are listed in the following Table I.

Examples 7 and 8

An aluminum plate was treated in the same manner used in Examples 1 to 3 till the formation of a porous anodized layer.

Then the anodized aluminum plate was immersed in a 0.1% aqueous solution of Aluminium Yellow G3LW (Ex. 7) and Aluminium Gray NL (Ex. 8) (both available from Sandoz A.G.) maintained at 30 ° C for 20 seconds and then washed with water. The plate was treated in a chamber saturated with water vapor at 100 ° C, 1 atm. for 30 seconds to give a substrate. Then the extent of dyeing thereof was determined, followed by application of a light-sensitive solution having the following composition and drying to thus form a light-sensitive layer. The coated amount of the light-sensitive layer was 2.5 g/m² (weighed after drying).

Component	Amount (part by weight)
ester compound of naphthoquinone(1,2)-diazido-(2)-5-sulfonic acid chloride and resorcin/benzaldehyde resin	1
copolycondensed resin of phenol/m- and p-cresol mixture/formaldehyde	3.5
2-trichloromethyl-5-[β -(2'-benzofuryl)vinyl]-1,3,4-oxadiazole	0.03
Victoria Pure Blue BOH (available from HODOGAYA CHEMICAL CO., LTD.)	0.1
o-naphthoquinonediazidesulfonic acid ester of p-butyl-phenol/benzaldehyde novolak resin	0.05
methyl cellosolve	27

The PS plates thus prepared were exposed to light from a 3 KW metal halide lamp for 50 seconds at a distance of 1 m, through a Fuji Film Step Guide and a K-value Film available from FOGRA CO., LTD. using a vacuum printing frame, then developed with a 4% aqueous solution of sodium metasilicate at 25 ° C for 45 seconds, gummed-up with an aqueous solution of gum arabic to thus give lithographic printing plates.

The half tone dot reproduction of the resulting lithographic printing plates was determined. The results observed are summarized in Table II given below.

Comparative Example 6

Substrates were prepared in the same manner used in Examples 7 and 8 except that the dyeing treatment with a dye or the sealing treatment was omitted, the extend of dyeing was determined and then the substrate was subjected to a silicate treatment followed by application of a light-sensitive layer, exposure to light, a developing treatment and gumming-up treatment to thus give a lithographic printing plate as in the same manner used in Examples 7 and 8.

The half tone dot reproduction of the resulting lithographic printing plate was determined. The result obtained is listed in the following Table II.

As seen from the foregoing results, the lithographic printing plate obtained by exposing, to light, a PS plate in which the substrate prepared by the metod of this invention is used and then developing the exposed PS plate has various properties superior to those for the lithographic printing plate obtained according to conventional methods in which the substrate is not subjected to dyeing treatment or subjected to dyeing treatment without performing any sealing treatment. For instance, the former has no contamina-

tion of the non-image areas during printing and is excellent in half tone dot reproduction.

Table I: Quality of Negative-Working PS plate

5	Ex. NO.	Dyeing (time)	Sealing	Hydrophi- lization	Contamination of non-image areas ¹⁾	Half Tone Dot Reproduction ²⁾	Extent of Dyeing ³⁾
10	1	Yes (10'')	Yes	Yes	A	12 μ	0.10
	2	Yes (20'')	Yes	Yes	A	10 μ	0.15
15	3	Yes (30'')	Yes	Yes	A	8 μ	0.20
	4	Yes (20'')	Yes	Yes	A	10 μ	0.15
	5	Yes (20'')	Yes	Yes	A	10 μ	0.15
20	6	Yes (20'')	Yes	Yes	A	10 μ	0.15
	Comp. Ex.						
25	.1	Yes (20'')	None	Yes	C	15 μ	0 *

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	2	None	None	Yes	C	15 μ	0
	3	None	Yes	Yes	B	15 μ	0
5	4	Yes ⁴⁾	None	Yes	B	12 μ	0.15
	5	Yes (20'')	None	None	C	12 μ	0.15

10 1): After the application of a light-sensitive layer, the PS plate was allowed to stand under high temperature and high humidity conditions for several days and then exposed to light and developed to obtain a lithographic printing plate. Printing operation was performed using the lithographic printing plate thus obtained to form printed matters and background contamination thereof was evaluated according to the following three stage evaluation standard:

- 25 A : There was not observed any contamination with ink;
 B : The printed matters were slightly contaminated with ink;
 C : The printed matters were greatly contaminated with ink.

30 2): The half tone dot reproduction is expressed in the smallest width of fine line which remains undefaced on the printed matters when the printing operation is performed using a lithographic printing plate printed out through the K-value film available from FOGRA CO., LTD.
 35 The smaller the value, the higher the half tone dot reproduction.

3): The extent of dyeing ΔD is defined as follows:

40 $\Delta D =$ (The maximum reflective optical density of the substrate prior to the application of the light-sensitive layer determined at 350 to 450 nm) - (the maximum reflective optical density of the substrate prior to the dyeing determined at 350 to 450 nm).

The maximum reflective optical density of the substrate was determined with an UV - visible light spectrophotometer.

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4): The coated amount of each dye was 10 mg/m².

55 *: The substrate was dyed, but the color was disappeared when it was subsequently dipped in an aqueous solution of sodium silicate.

Table II

Quality of Positive-Working PS plate				
Ex. No.	Dyeing (time)	Sealing	Half Tone Dot Reproduction ⁵⁾	Extent of Dyeing ³⁾
7	Yes (20")	Yes	6μ	0.15
8	Yes (20")	Yes	6μ	0.15
Comp. Ex. 6	None	None	10μ	0

5): The half tone dot reproduction is expressed in the smallest width of fine line which remains undefaced on the printed matters when the printing operation is performed using a lithographic printing plate printed out through the K-value film available from FOGRA CO., LTD. The smaller the value, the higher the half tone dot reproduction.

Claims

1. A method for producing a substrate for a presensitized plate for use in making a lithographic printing plate which comprises surface-roughening and anodizing an aluminum plate, wherein the surface-roughened and anodized aluminum plate is then, in order, subjected to the following treatments:

(a) a dyeing treatment with a dye; and

(b) a sealing treatment.

2. The method of claim 1 wherein the dyeing treatment is carried out by spraying or coating an aqueous solution of a dye on the aluminum plate or by dipping the plate in an aqueous solution of a dye.

3. The method of claim 2 wherein the dye is an acidic dye or a direct dye.

4. The method of claim 2 wherein the dyeing treatment is performed by dipping the plate in an aqueous solution of a dye and the conditions for dyeing are a dye concentration ranging from 0.1 to 10 g/l, a dyeing temperature ranging from 20 to 70° C and a dyeing time ranging from 2 seconds to 2 minutes.

5. The method of claim 1 wherein the extent of the dyeing treatment ranges from 0.05 to 0.25 expressed in reflective optical density as determined at a wavelength of a light source for exposure.

6. The method of claim 1 wherein the dyeing treatment is performed with a dye which can provide gray-colored non-image areas.

7. The method of claim 6 wherein the dye which can provide gray-colored non-image areas is Aluminium Gray NL, Aluminium Black 2LW, Basarocks Black WL or Sanodal Deep Black MLW.

8. The method of claim 1 wherein the sealing treatment is performed by exposing the aluminum plate to steam under pressure or under normal pressure.

9. The method of claim 8 wherein the sealing treatment with steam is carried out at a relative humidity of not less than 70%, a steam temperature of not less than 95° C for 2 seconds to 2 minutes.

10. The method of claim 1 wherein the aluminum plate is further subjected to hydrophilization treatment after the sealing treatment.

11. The method of claim 10 wherein the hydrophilization treatment is performed with an alkali metal silicate, potassium fluorozirconate or a polyvinylsulfonic acid.

12. The method of claim 10 wherein a hydrophilic underlying coating is applied to the aluminum plate after the sealing and hydrophilization treatments.

13. The method of claim 1 wherein a hydrophilic underlying coating is applied to the surface of the aluminum plate after the sealing treatment.

14. The method of claim 1 wherein the aluminum plate is subjected to an alkali etching treatment and a neutralization treatment after the surface-roughening treatment.

15. The method of claim 1 wherein the anodization is performed using sulfuric acid as an electrolyte.

16. The method of claim 1 wherein the amount of the anodized layer ranges from 0.1 to 10 g/m².

17. The method of claim 16 wherein the amount of the anodized layer ranges from 1 to 6 g/m².

18. A presensitized plate which comprises a support prepared by the method of claim 1 and a lithographically suitable light-sensitive layer provided on the support.

19. A presensitized plate which comprises a support prepared by the method of claim 13 and a positive

working light-sensitive layer containing an o-naphthoquinonediazide compound on the support.

20. A presensitized plate which comprises a support prepared by the method of claim 12 and a negative working light-sensitive layer containing a diazo resin and a binder, on the support.

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