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W-8000 München 22(DE)**(54) **Substrate for lithographic printing plate.**

(57) A substrate for lithographic printing plate comprises an rolled aluminum plate whose specular gloss determined by making light incident upon the aluminum plate perpendicularly to the rolling direction of the rolled plate is at least 70% of that determined by making light incident upon the rolled plate parallel to the rolling direction of the rolled plate. The lithographic printing plate obtained from the substrate can output the rate of area of the plate occupied by patterns almost equal to the true area occupied by the patterns even if the lithographic printing plate is put on a printing press in such a manner that the rolling direction of the aluminum substrate of the printing plate is perpendicular to the direction of the vector component, parallel to the surface of the substrate, of the incident light from a light source of a plate scanner.

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## BACKGROUND OF THE INVENTION

The present invention relates to a substrate for presensitized plate for use in making a lithographic printing plate (hereinafter referred to as "PS plate") and hence for lithographic printing plate and in particular, to a substrate for PS plate or lithographic printing plate which can show improved suitability for a plate scanner of an ink-presetting system.

The PS plate comprising an aluminum substrate is in general imagewise exposed to light, developed with a developer and then subjected to retouching to give a lithographic printing plate. The resulting printing plate is put on a printing press to perform printing operations.

The basic principle of the offset printing is to express light and shade of patterns in terms of the difference between the numbers of half-tone dots and, therefore, it is ideal that the half-tone dot portion having a rate of area occupied by the half-tone dots of 10% and solid portion printed on paper should have the same ink thickness. Moreover, the amount of ink consumed during the offset printing depends on the area occupied by patterns and correspondingly it is necessary to read the rate of area occupied by the patterns for every key pitch of an ink bottle and to control the switching (or opening and closing) of the ink key depending on the outputted value of the rate. For this reason, an ink-presetting system is in general used for controlling the switching of the ink key. The "ink-presetting system" herein means a system for reading the rate of the area of a lithographic printing plate occupied by patterns for every key pitch by a plate scanner prior to the fitting of the printing plate to a printing press and for automatically controlling the switching of the ink key depending on the rate observed. The application of such a system makes it possible to substantially reduce the time required for adjusting the amount or thickness of ink and to improve productivity.

The reading of the rate of area of a lithographic printing plate occupied by patterns is generally carried out by the following method using a plate scanner. The method comprises the steps of irradiating the plate surface with light from a light source arranged perpendicularly to the scanning direction, detecting or determining the quantity of light reflected from the surface of an aluminum plate on the non-image area by photosensors arranged on a linear line parallel to the light source and calculating the area occupied by light-absorbing image area to thus determine the rate of area occupied by the patterns.

However, in case of lithographic printing plate comprising an aluminum plate as a substrate, the following disadvantages are observed when reading the rate of the area occupied by patterns. The aluminum plate has stripes (rolling marks) on the surface along the rolling direction and hence the light incident upon the surface is scattered within the planes perpendicular to the rolling marks. Thus, the light which is made incident upon the aluminum plate perpendicularly to the rolling direction thereof is scattered back and forth (parallel direction) relative to the direction of the light propagation. Therefore, the quantity of light detected by a method capable of detecting only the light within a limited angle of reflection is smaller than that observed when any scattering by the rolling marks is not caused. On the other hand, the light which is made incident upon the aluminum surface parallel to the rolling direction thereof is scattered and spreads towards the directions perpendicular to the direction of light propagation due to the presence of the rolling marks, but the resulting quantity of light detected is almost the same as that observed for the aluminum plate free of rolling marks if the quantities of light detected by all of the photosensors are integrated, since many light sources are arranged in this direction.

As has been explained above, when reading the rate of the area of a lithographic printing plate occupied by patterns using a plate scanner and putting the printing plate on a printing press in such a manner that the rolling direction of the aluminum plate of the printing plate is perpendicular to the direction of the vector component, parallel to the substrate surface, of the incident light from the light source of a plate scanner, the quantity of reflected light is lowered and, therefore, a rate of area occupied by the patterns greater than the true value would be outputted from the scanner.

To solve this problem, there have been proposed various methods for eliminating the rolling marks remaining on the surface of an aluminum substrate. Examples of such methods include those comprising surface roughening treatments, for instance, mechanical methods such as brush graining and ball graining; and electrochemical methods such as electrolytic graining; and a combination of these two methods. However, these treatments make the manufacturing process complicated and lead to an increase in the production cost.

Further, the rolling marks are masked by, for instance, dispersion of titanium oxide powder in a light-sensitive layer and/or a primer layer for a lithographic printing plate requiring no dampening water, but a large amount of titanium oxide must be dispersed in the layers to mask the rolling marks and this makes the installation for dispersing the same complicated and expensive.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a substrate for PS plates or lithographic printing plates which can provide a lithographic printing plate capable of outputting the rate of area of the plate occupied by patterns almost equal to the true area occupied by the patterns even if, when determining the rate of the area occupied by patterns using a plate scanner of an ink presetting system, the lithographic printing plate is put on a printing press in such a manner that the rolling direction of the aluminum substrate of the printing plate is perpendicular to the direction of the vector component, parallel to the substrate surface, of the incident light from light sources of the plate scanner.

The inventors of this invention have conducted various studies to achieve the foregoing object and have completed the present invention. Consequently, the present invention relates to a substrate for lithographic printing plates which comprises an aluminum plate whose specular gloss determined by making light incident upon the aluminum plate perpendicularly to the rolling direction of the plate is at least 70% of that determined by making light incident upon the plate parallel to the rolling direction.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will hereunder be explained in more detail on the basis of preferred embodiments.

Substrate

The aluminum plate used in the present invention as a material for making the substrate for lithographic printing plates must have the specular gloss determined by making light incident upon the aluminum plate perpendicularly to the rolling direction of the plate is at least 70% of that determined by making light incident upon the plate parallel to the rolling direction.

The term "specular gloss" herein means the value  $G_s(\theta)$  represented by the following equation (I) and can be determined by, for instance, Glossmeter VG-1D available from Nippon Denshoku Kogyo K.K.

$$G_s(\theta)(\%) = (\phi_s / \phi_{os}) \times (\text{gloss of Reference Surface Used}) \quad (I)$$

$\theta$  : angle of incident light (in the invention, the measurement was carried out at a  $\theta$  of  $60^\circ$ )

$\phi_s$  : specular reflection light flux from the sample surface

$\phi_{os}$  : specular reflection light flux from the reference surface

$G_s(\theta)$  : specular gloss

The aluminum plate used in the invention as a material for the substrate used for lithographic printing plates is a plate-like material mainly comprising aluminum such as those comprising pure aluminum or those comprising an aluminum alloy containing a small amount of foreign atoms. Examples of the foreign atoms are silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium. The content of these foreign atoms in the aluminum alloys is in the order of up to about 10% by weight. Aluminum preferably used in the present invention is pure aluminum, but it is very difficult to produce completely pure aluminum from the viewpoint of the refining technique. Therefore, preferably used are those comprising foreign atoms as low as possible and the aluminum alloys having the foreign atom content defined above can be used in the present invention as materials for preparing the substrate without any problem. As explained above, the composition of the aluminum plates usable in the present invention is not restricted to specific one and hence those obtained from conventionally known or currently used materials can arbitrarily be employed.

The aluminum plate used in the invention is usually produced by the rolling technique and in general has a thickness ranging from 0.1 to 0.5 mm. The specular gloss of the aluminum plate is greatly dependent upon the rolling rolls used in the rolling process and the rolling rolls are thus very important in the present invention. In particular, the surface roughness of the rolling rolls is most important and preferably those having an averaged central line surface roughness ( $R_a$ ) of not more than  $0.1 \mu\text{m}$ , more preferably not more than  $0.05 \mu\text{m}$  are used. The aluminum plate obtained by rolling with rolls having such a surface roughness has a surface roughness ( $R_a$ ) ranging from 0.1 to  $0.01 \mu\text{m}$ .

If rolling rolls having a surface roughness of more than  $0.1 \mu\text{m}$  are used, the specular gloss determined by making light incident upon the aluminum plate perpendicularly to the rolling direction of the plate is less than 70% of that determined by making light incident upon the plate parallel to the rolling direction.

Accordingly, if the rate of area occupied by patterns is determined by a plate scanner, the plate scanner outputs a value greater than the true rate and, therefore, the resulting aluminum plate cannot be used in the present invention.

The aluminum plate thus obtained is degreased and then desired coating layers can directly be applied thereto, but the surface of the plate may further be treated prior to the application of the coating layers.

#### Surface Treatments

A rolling oil is adhered to the surface of the rolled aluminum plate and hence the plate must be degreased. The degreasing treatment is performed by the use of an alkali such as caustic soda, caustic potash, sodium carbonate, sodium phosphate and sodium silicate. Preferred conditions for degreasing are a temperature ranging from 30 to 100 ° C, an alkali concentration ranging from 1 to 50% and a treating time ranging from 1 to 100 seconds.

After such a degreasing treatment, coating layers such as a light-sensitive layer may directly be applied to the aluminum plate, but the plate may be subjected to other surface treatments such as graining, anodization and/or hydrophilization treatments prior to the application of the coating layers. Preferred graining treatments are, for instance, sand blasting or liquid honing methods in which an abrasive is blown on the plate surface, a brush graining method in which the aluminum surface is rubbed with a brush and wet abrasive particles and an electrolytic graining carried out in an electrolyte such as nitric acid or hydrochloric acid, which may, if necessary, be used in combination. The grained plate surface is cleaned with an acid or alkali and then anodized. The anodization treatment is in general performed in an electrolyte comprising sulfuric acid, but it may also be performed in an electrolyte such as those comprising phosphoric acid or a mixed acid of sulfuric acid and phosphoric acid. Preferred conditions for the anodization are not always particularly specified, but are in general an electrolyte concentration ranging from 1 to 30% by weight, a temperature ranging from 20 to 50 ° C, an anodization time ranging from 5 to 100 seconds and a current density ranging from 5 to 100 A/dm<sup>2</sup>.

After forming a desired anodized layer, the aluminum plate may be hydrophilized by immersing it into a sodium silicate solution. Other hydrophilization treatments may also be used and examples thereof are immersion in a fluorozirconate solution, a polyacrylate solution and a polyvinylphosphonate solution. Preferred conditions for the hydrophilization treatment are a concentration ranging from 1 to 20% by weight, a temperature ranging from 20 to 80 ° C and a treating time ranging from 5 to 30 seconds.

Various kinds of lithographic printing plates can be prepared by applying a variety of layers onto the surface of the thus treated aluminum substrate of the present invention for use in making lithographic printing plates.

Specific examples of such lithographic printing plates will be described below, but the present invention is by no means limited to these specific examples.

#### [I] PS Plate

PS plates comprise a substrate provided thereon with a light-sensitive layer. The light-sensitive layer is imagewise exposed to light directly through an original or through a film by the usual photomechanical method. Thereafter, the imagewise exposed light-sensitive layer is developed with a developer such as an organic solvent or an alkali solution to thus give ink-receptive image portions and hydrophilic non-image portions to hence give a lithographic printing plate.

The light-sensitive layer may be obtained from various kinds of light-sensitive composition. Specific examples thereof will be described below, but the present invention is by no means limited to these specific examples.

#### (1) Light-sensitive Layer Comprising Diazo Resin and Binder

Preferred examples of negative-working light-sensitive diazo compounds useful in the invention are such a reaction product of a diazonium salt with an organic condensation agent having reactive carbonyl group, e.g., aldol or acetal as a condensation product of diphenylamine-p-diazonium salt and formaldehyde (so-called light-sensitive diazo resins) disclosed in U.S. Patent Nos. 2,063,631 and 2,667,415. Examples of other useful condensed diazo compounds are such as those disclosed in U.S. Patent No. 3,679,419 and U.K. Patent Nos. 1,312,925 and 1,312,926. The light-sensitive diazo compounds of this type are in general available in the form of water-soluble inorganic salts and therefore, they can be applied as an aqueous solution. Alternatively, it is also possible to use substantially water-insoluble light-sensitive diazo resins

obtained by reacting these water-soluble diazo compounds with aromatic or aliphatic compounds having either one or both of at least one phenolic hydroxyl group and sulfonic acid group in the manner as disclosed in U.K. Patent No. 1,280,885.

In addition, they may be used as a reaction product with hexafluorophosphates or tetrafluoroborates as disclosed in J.P. KOKAI No. 56-121031. Besides, diazo resins as disclosed in U.K. Patent No. 1,312,925 are also preferred in the present invention.

Examples of the compounds having phenolic hydroxyl group are hydroxybenzophenone, 4,4-bis-(4'-hydroxyphenyl)pentanoic acid, resorcinol, and diphenolic acids such as diresorcinol, which may have substituents other than the phenolic hydroxyl group. The term "hydroxybenzophenone is herein defined to include 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2,2',4,4'-tetrahydroxybenzophenone. Examples of preferred sulfonic acids include aromatic sulfonic acids such as sulfonic acids of benzene, toluene, xylene, naphthalene, phenol, naphthol and benzophenone or soluble salts thereof such as ammonium salts and alkali metal salts. The compounds having a sulfonate group may in general be substituted with a lower alkyl group, a nitro group, a halo group, and/or another sulfonate groups. Preferred examples thereof 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, alizarin-sulfonic acid, o-toluidine-m-sulfonic acid and ethanesulfonic acid. Sulfuric acid esters of alcohols or aromatic hydroxy compounds or salts thereof are also preferably used. These compounds are usually available as anionic surfactants. Specific examples thereof are ammonium salts or alkali metal salts of lauryl sulfate, alkylaryl sulfates, p-nonylphenyl sulfate, 2-phenylethyl sulfate and isooctylphenoxy diethoxyethyl sulfate.

These substantially water-insoluble light-sensitive diazo resins can be isolated as precipitates by mixing an aqueous solution of a water-soluble light-sensitive diazo resin and approximately the same amount of an aqueous solution of the foregoing aromatic or aliphatic compound.

In addition, preferred are also include diazo resins disclosed in U.K. Patent No. 1,312,925.

The most preferred diazo resin is 2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate of a condensate of p-diazodiphenylamine and formaldehyde.

The content of the diazo resin in the light-sensitive layer preferably ranges from 5 to 50% by weight. As the content thereof is lowered, the light sensitivity of the resulting light-sensitive layer is correspondingly increased, but in contrast therewith, the stability with time thereof is lowered. The optimum content of the diazo resin ranges from about 8 to 20% by weight.

On the other hand, various polymeric compounds may be used as the binder of the light-sensitive composition, but in the present invention, preferably used are those carrying hydroxyl, amino, carboxyl, amido, sulfonamido, active methylene, thioalcohol and/or epoxy groups. Specific examples of the binders include schellac as disclosed in U.K. Patent No. 1,350,521; polymers mainly comprising 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 as 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; linear polyurethane resins disclosed in U.S. Patent No. 3,660,097; polyvinyl alcohol resins which are converted into phthalates, epoxy resins obtained by the condensation of bisphenol A and epichlorohydrin, polymers having amino groups such as polyaminostyrene and polyalkylamino(meth)acrylate, and cellulose derivatives such as cellulose acetate, cellulose alkyl ether and cellulose acetate phthalate.

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

## (2) Light-Sensitive Composition Comprising o-Quinonediazide Compound

Particularly preferred o-quinonediazide compounds are, for instance, o-naphthoquinonediazide compounds which are disclosed in a variety of publications, for instance, 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 and which are preferably used in the composition. Among these, preferred are o-naphthoquinonediazidosulfonic acid esters or o-naphthoquinonediazidocarboxylic acid esters of aromatic hydroxy compounds; o-naphthoquinonediazidosulfonic acid amides or o-naphthoquinonediazidocarboxylic acid amides of aromatic amino compounds and particularly, esterification reaction products of condensates of pyrogallol and acetone with o-naphthoquinonediazidosulfonic acid disclosed in U.S. Patent No. 3,635,709; esterification reaction

products of polyesters having hydroxyl groups at the ends with o-napht hoquinonediazidosulfonic acid or o-naphthoquinon ediazidocarboxylic acid disclosed in U.S. Patent No. 4,028,111; esterification reaction products of homopolymers of p-hydroxystyrene or copolymers of p-hydroxystyrene and monomers copolymerizable therewith, with o-naphthoquinonediazidosulfonic acid or o-naphthoquinonediazidocarboxylic acid disclosed in U.K. Patent No. 1,494,043; amidation reaction products of copolymers of p-aminostyrene and monomers copolymerizable therewith, with o-naphthoquinonediazidosulfonic acid or o-naphthoquinonediazidocarboxylic acid disclosed in U.K. Patent No. 3,759,711 are very preferable.

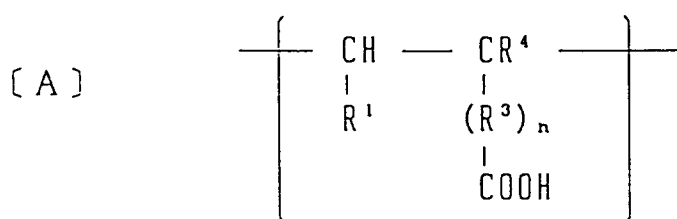
These o-quinonediazide compounds may be used alone, but are preferably used in combination with alkali-soluble resins. Preferred alkali-soluble resins include novolak type phenol resins and specific examples thereof are phenol-formaldehyde resins, o-cresol-formaldehyde resins, and m-cresol-formaldehyde resins. Moreover, it is more preferable to use condensates of phenols or cresols substituted with an alkyl group having 3 to 8 carbon atoms with formaldehyde such as t-butylphenol-formaldehyde resin simultaneously with the foregoing phenol resins as disclosed in U.S. Patent No. 4,123,279. The composition for forming the light-sensitive layer may comprise these alkali-soluble resins in an amount ranging from about 50 to about 85% by weight, preferably 60 to 80% by weight on the basis of the total weight of the composition.

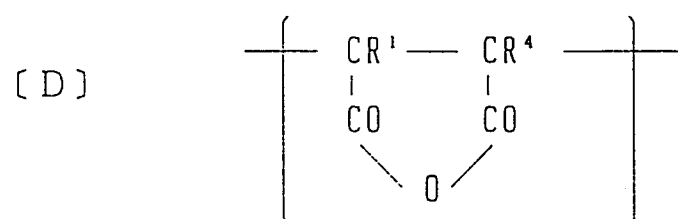
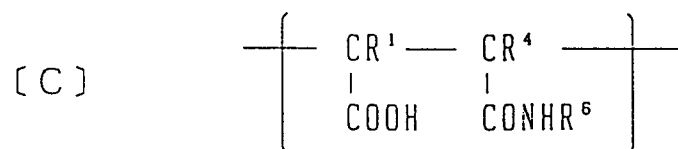
The light-sensitive composition comprising o-quinonediazide compounds may, if necessary, comprise other components such as dyes, plasticisers and compounds capable of imparting printing out properties to the resulting light-sensitive layer as disclosed in U.K. Patent Nos. 1,401,463 and 1,039,475 and U.S. Patent No. 3,969,118.

(3) Light-sensitive Layer Obtained from Composition Comprising Polymer Having Carboxylic Acid or Carboxylic Acid Anhydride Residues, Addition-polymerizable Unsaturated Compound and Photopolymerization Initiator

The lithographic printing plate which comprises a substrate provided with a layer of the composition comprising a polymer having carboxylic acid residues or carboxylic anhydride residues, an addition-polymerizable unsaturated compound and a photopolymerization initiator is excellent in storability, the exposed aluminum plate surface on the non-image area is hardly contaminated with a printing ink, has good hydrophilicity capable of rapidly removing ink stains on the non-image area and the aluminum plate has high adhesion to the light-sensitive layer.

As the polymer having carboxylic acid residues or carboxylic anhydride residues, preferred are those having the structural units selected from the group consisting of those represented by the following general formulae (A) to (D):





In the general formulas (A) to (D), R<sup>1</sup> and R<sup>4</sup> each represents a hydrogen atom or an alkyl group; R<sup>3</sup> represents a phenylene group or an alkylene group optionally having a hydroxyl group; R<sup>5</sup> represents a hydrogen atom or an alkyl group optionally having substituents; R<sup>6</sup> represents an alkyl, allyl, aryl or cycloalkyl group which may have substituents; and n is an integer of 0 or 1.

More specifically, examples of the repeating units represented by formula (A) are those derived from acrylic acid, methacrylic acid, crotonic acid and vinyl benzoic acid; examples of the repeating units represented by formula (B) those derived from maleic acid, maleic acid monohydroxyalkyl ester and maleic acid monocyclohexyl ester; examples of the repeating units of formula (C) those derived from maleic acid monoalkylamide and maleic acid monohydroxyalkylamide; and examples of the repeating units represented by formula (D) those derived from maleic anhydride and itaconic anhydride. As the polymers, those having an average molecular weight ranging from 1,000 to 100,000 are usually used in the invention.

The addition polymerizable unsaturated compounds herein mean monomers having ethylenically unsaturated double bonds which can cause addition polymerization between them in the three-dimensional direction when the photopolymerizable light-sensitive composition is irradiated with actinic rays. Examples thereof are unsaturated carboxylic acids, esters of unsaturated carboxylic acids and aliphatic polyhydric compounds and esters of unsaturated carboxylic acids and aromatic polyhydric compounds.

As the photopolymerization initiators, there may be mentioned, for instance, benzoin, benzoin alkyl ether, benzophenone, anthraquinone and Michler's ketones which may be used alone or in combination in an amount ranging from 1 to 3 g/m<sup>2</sup> (weighed after drying).

## [II] Presensitized Plate for Use in Making Lithographic Printing Plate Requiring No Dampening Water (Hereunder Referred to as "PS Plate Requiring No Dampening Water")

There have already been proposed various PS plates requiring no dampening water in which a silicone rubber layer serves as a non-image area (see, for instance, Japanese Examined Patent Publication (hereinafter referred to as "J.P. KOKOKU") Nos. Sho 44-23042, Sho 46-16044, Sho 54-26923 and Sho 61-54222 and Japanese Unexamined Patent Publication (Hereinafter referred to as "J.P. KOKAI") No. Sho 63-265247).

There are two kinds of methods for preparing a PS plate requiring no dampening water of this type. One of these is disclosed in, for instance, J.P. KOKOKU No. Sho 46-16044 in which image areas are formed by dissolving the light-sensitive layer on the image areas with a developer to thus remove the

silicone rubber layer on the image areas and the other is disclosed in, for instance, J.P. KOKOKU No. Sho 54-26923 and J.P. KOKAI No. 56-80046 in which a PS plate requiring no dampening water comprising a photoadhesive or photopeelable light-sensitive layer and a silicone rubber layer is employed and the silicone rubber layer on image areas is selectively removed.

5 In the former, i.e., in the method wherein the image areas are formed by dissolving the light-sensitive layer on the image areas with a developer, it is preferred to apply a silicone rubber layer having a thickness ranging from 0.5 to 5  $\mu\text{m}$  on the photopolymerizable light-sensitive layer of the foregoing polymer having carboxylic acid residues or carboxylic acid anhydride residues, an addition-polymerizable unsaturated compound and a photopolymerization initiator.

10 If the latter and in particular, a PS plate requiring no dampening water which comprises a photoadhesive light-sensitive layer and a silicone rubber layer is exposed to light, the photoadhesive light-sensitive layer is firmly photolytically adhered to the silicone rubber layer. Thus, making the most use of this phenomenon, only the silicone rubber layer on the non-exposed areas can be selectively peeled off and removed with a developer which does not substantially dissolve the photoadhesive light-sensitive layer (only slightly dissolves the layer) and is capable of swelling the light-sensitive layer and/or the silicone rubber layer. The exposed light-sensitive layer thus serves as an ink-receptive portion of the printing plate. In this case, the silicone rubber layer is preferably applied onto the light-sensitive layer comprising a component substantially insoluble in a developer, an addition-polymerizable unsaturated compound and a photopolymerization initiator in a thickness ranging from 0.5 to 5  $\mu\text{m}$ .

20 The effect of the present invention is particularly conspicuous in this embodiment, i.e., in the PS plate requiring no dampening water, since the surface of the aluminum substrate is not generally subjected to any surface roughening treatment (the rolling marks are reduced or disappeared through the surface roughening treatment).

### 25 [III] PS Plate for Electrophotographic Plate-Making Process

The electrophotographic plate making method has been known and is detailed in "DENSHI SHASHIN GIJUTSU NO KISO TO OYO (The Basis and Applications of Electrophotographic Techniques), issued by Society of Electrophotography, published by Corona Publishing Company (1988) of "KIROKU ZAIRYO 30 MANUAL (A Manual of Recording Materials", Trykepus Publishing Company (1981) which may be used in the invention.

For instance, there has been known a method which comprises applying, onto an aluminum substrate, a photoconductive layer comprising at least a photoconductive material and an alkali-soluble resin, developing with a toner, fixing the toner and then removing the photoconductive layer on non-image area free of toner 35 with an alkaline solution in the usual manner to give a lithographic printing plate.

Specific examples thereof are those disclosed in J.P. KOKOKU Nos. Sho 37-17162, Sho 38-6961, Sho 38-7758, Sho 41-2426 and Sho 46-39405 and J.P. KOKAI Nos. Sho 50-19509, Sho 50-19510, Sho 52-2437, Sho 54-145538, Sho 54-134632, Sho 55-105254, Sho 55-153948, Sho 55-161250, Sho 57-147656 and Sho 57-161863.

40 Moreover, it is also possible to use a method which comprises transferring the toner image formed on an electrophotographic light-sensitive material onto a proper substrate to give a lithographic printing plate.

For instance, toner images are formed on an organic or inorganic electrophotographic light-sensitive material in the usual manner. The resulting toner images are transferred to an aluminum substrate in the usual known transfer method such as a corona transfer, bias-roller transfer or pressure transfer method to 45 give a lithographic printing plate. In addition, the toner images can, if necessary, be transferred to an aluminum substrate after a plurality of transferring processes through a transferring material such as a rubber roller.

Further, a lithographic printing plate may also be prepared by previously applying an insulating layer onto an aluminum substrate, then transferring toner images to the insulating layer in the usual manner and 50 removing the non-image area free of toner.

This method is detailed in, for instance, J.P. KOKAI Nos. Sho 59-36272, Sho 60-107042, Sho 61-118778, Hei 1-225975 and Hei 1-216367 and J.P. KOKOKU No. Sho 55-42752.

The lithographic printing plate obtained from the substrate therefor of the present invention can output the rate of area of the printing plate occupied by patterns almost equal to the true area of the patterns 55 formed thereon even if, when determining the rate of the area occupied by patterns using a plate scanner of an ink presetting system, the lithographic printing plate is put on a printing press in such a manner that the rolling direction of the aluminum substrate of the printing plate is perpendicular to the direction of the vector component, parallel to the substrate surface, of the incident light from light sources of the plate scanner.



The present invention will be explained in more detail with reference to the following non-limitative working Examples and the effect practically attained by the present invention will also be discussed in detail in comparison with Comparative Examples.

#### 5 Example 1

An aluminum plate (JIS A1050; surface roughness = 0.04  $\mu\text{m}$ ) which had been rolled with rolls having an averaged center line surface roughness (Ra) of 0.03  $\mu\text{m}$  was immersed in a 10% aqueous solution of NaOH at 50° C for 20 seconds to remove the rolling oil from the surface thereof and then immersed in a  
10 2.5% aqueous solution of No. 3 sodium silicate at 70° C for 10 seconds to give an aluminum substrate.

The rate of specular gloss of the foregoing rolled aluminum plate (JIS A1050) was determined by a glossmeter VG-1D available from Nippon Denshoku Kogyo K.K. The results thus obtained are summarized in the following Table 1. The rate of specular gloss is defined as follows:

$$15 \text{ Rate of Specular Gloss(\%)} = (\text{S.G.})_v \times 100/(\text{S.G.})_p$$

(S.G.)<sub>v</sub> : specular gloss determined by making light incident upon the surface vertically to the rolling direction.

20 (S.G.)<sub>p</sub> : specular gloss determined by making light incident upon the surface parallel to the rolling direction.

A light-sensitive layer was formed on the surface of the aluminum substrate thus obtained by applying a light-sensitive solution having the following composition in an amount of 2.0 g/m<sup>2</sup>(weighed after drying) and then drying.

25

#### Light-sensitive Solution

30

Component	Amount (part by weight)
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N-(4-hydroxyphenyl)methacrylamide/2-hydroxy-	5.0
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35

ethyl methacrylate/acrylonitrile/methyl	
---	--

methacrylate/methacrylic acid (molar ratio	
--	--

40

= 15/10/30/38/7) copolymer (average molecular weight = 60,000)	
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hexafluorophosphate of condensate of 4-diazo-	0.5
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45

diphenylamine and formaldehyde	
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phosphorous acid	0.05
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50

Victoria Pure Blue BOH (available from Hodogaya	0.1
---	-----

Chemical Co., Ltd.)	
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2-methoxyethanol	100
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The PS plate thus prepared was imagewise exposed to light in a vacuum printing frame by making the surface of the plate and an original having a rate of area occupied by half-tone dots of 50% at a density of

133 lines/inch and then irradiating the assembly with light from a 3 KW metal halide lamp for 50 seconds at a distance of 1 m, then developed with a developer having the following composition and gummed-up with an aqueous solution of gum arabic to give a lithographic printing plate.

Developer	
Component	Amount (part by weight)
sodium sulfite	5
benzyl alcohol	30
sodium carbonate	5
sodium isopropyl naphthalenesulfonate	12
pure water	1000

The resulting lithographic printing plate was subjected to test for examining suitability for plate scanner of an ink presetting system. The results obtained are summarized in Table 1.

The term "suitability for plate scanner" herein means the ability of outputting the rate of area of a lithographic printing plate occupied by patterns almost equal to the true area occupied by the patterns even if the lithographic printing plate is put on a printing press in such a manner that the rolling direction of the aluminum substrate of the printing plate is perpendicular to the direction of the vector component, parallel to the substrate surface, of the incident light from the light source of the plate scanner. Therefore, the smaller the difference between the rates of the area occupied by patterns each observed when the rolling direction is perpendicular to or parallel to the direction of the vector component, parallel to the substrate surface, of the incident light, the higher the suitability for plate scanner.

#### Comparative Example 1

An aluminum plate (JIS A1050; surface roughness =  $0.20\ \mu\text{m}$ ) which had been rolled with conventional rolls having an averaged center line surface roughness of  $0.2\ \mu\text{m}$  was immersed in a 10% aqueous solution of NaOH at  $50^\circ\text{C}$  for 20 seconds to remove the rolling oil from the surface thereof and then immersed in a 2.5% aqueous solution of No. 3 sodium silicate at  $70^\circ\text{C}$  for 10 seconds to give an aluminum substrate.

The rate of specular gloss of the foregoing rolled aluminum plate (JIS A1050) was determined in the same manner used in Example 1. The results thus obtained are summarized in Table 1.

The suitability for plate scanner of the lithographic printing plate produced in the same manner used in Example 1 was likewise determined and the results obtained were summarized in Table 1.

#### Example 2

To an aluminum substrate prepared in the same procedures used in Example 1, there were applied, in order, a primer layer, a light-sensitive layer and a silicone rubber layer in the following manner to give an original PS plate requiring no dampening water.

##### o Primer Layer

The primer layer was formed by applying a composition for primer layer having the following composition onto the surface of the resulting aluminum substrate in an amount of  $8.0\ \text{g/m}^2$  (weighed after drying) and then heating at  $120^\circ\text{C}$  for 3 minutes to dry the same.

##### Composition for Primer Layer

A solution comprising 450 parts by weight of pure water and 2.6 parts by weight of anhydrous sodium carbonate was heated to  $70^\circ\text{C}$  and 50 parts by weight of casein powder (casein lactate (New Zealand-grown product; available from Murray Coulburn Cooperative Co., Ltd.)) was added to and dissolved in the solution with stirring and then the following components were incorporated into the aqueous casein solution to give a composition for primer layer:

Component	Amount (part by weight)
SBR latex (Nipol LX110 (solid content: 40.5%; T <sub>g</sub> = -60 °C ; available from Nippon Zeon Co., Ltd.)	50 (reduced solid content)
Quinoline Yellow -WS (yellow dye; available from Chugai Kasei Co., Ltd.)	0.5
Nikkol OTP-100S (anionic surfactant; available from Nikko Chemicals Co., Ltd.)	1.2
γ -glycidoxypopyltrimethoxysilane	3.0
CH <sub>2</sub> =CHSO <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> SO <sub>2</sub> CH=CH <sub>2</sub>	3.0
pure water	100

25 o Light-Sensitive Layer

Then a light-sensitive layer was formed on the resulting primer layer by applying a light-sensitive composition having the following composition in an amount of 3.0 g/m<sup>2</sup> (weighed after drying) and drying at 100° C for one minute.

Light-Sensitive Composition

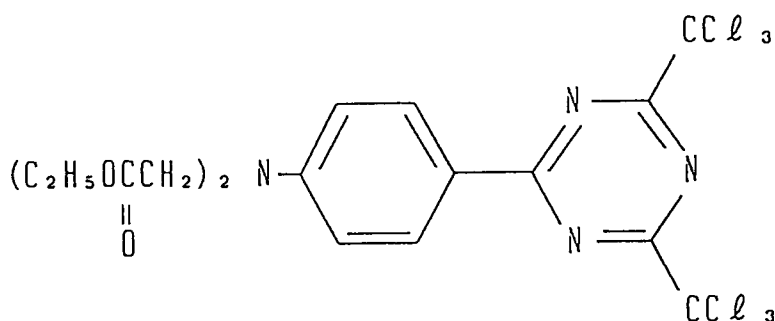
Component	Amount (part by weight)
-----------	-------------------------

2-allyloxyethyl methacrylate/2-methacryloxy	2
---	---

hydrogen succinate (90/10 mole%) copolymer	
--	--

$(\text{CH}_2=\text{CHCOOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2)_2-\text{CHOH}$	0.3
---	-----

compound of the following formula:	0.2
------------------------------------	-----



Phenol Cresol Blue (pH indicator)	0.01
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Diffencer MCF 323 (available from Dainippon Ink & Chemicals, Incorporated)	0.02
---	------

PF <sub>6</sub> salt of p-diazodiphenylamine/formaldehyde condensate	0.02
---	------

propylene glycol monomethyl ether	15
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methyl ethyl ketone	10
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## o Silicone Rubber Layer

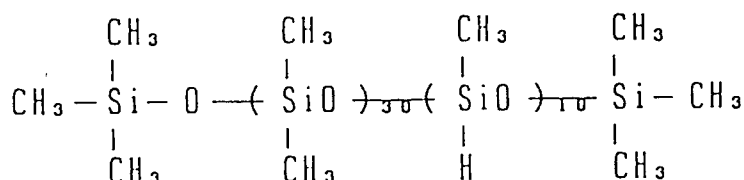
A silicone rubber layer was formed on the resulting light-sensitive layer by applying a composition for silicone rubber layer having the following composition in an amount of 2.0 g/m<sup>2</sup> (weighed after drying) and then drying at 140° C for 2 minutes to harden the layer.

Composition for Silicone Rubber Layer

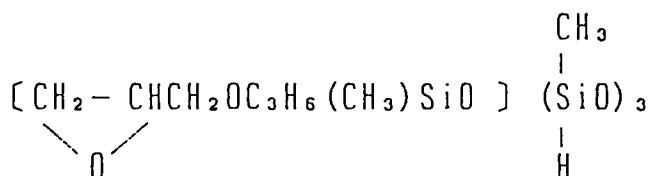
Component	Amount (part by weight)
-----------	-------------------------

siloxane (degree of polymerization = about 700)	9
---	---

compound of the following formula:	1
------------------------------------	---



compound of the following formula:	0.2
------------------------------------	-----



polydimethylsiloxane (degree of polymerization =	0.5
--	-----

about 8,000)	
--------------	--

olefin-chloroplatinic acid	0.2
----------------------------	-----

polymerization-inhibiting agent	0.15
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Isopar G (available from ESSO Chemical Company)	140
---	-----

A one-side matted polypropylene film having a thickness of 9  $\mu\text{m}$  was laminated with the surface of the silicone rubber layer thus produced to give an original PS plate requiring no dampening water.

The original PS plate requiring no dampening water thus prepared was imagewise exposed to light in a vacuum printing frame by making the surface of the plate come in close contact with an original having a rate of area occupied by half-tone dots of 50% at a density of 133 lines/inch and then irradiating the assembly with light from a 3 KW metal halide lamp for 50 seconds at a distance of 1 m, then the laminate film was peeled off, the exposed PS plate was developed by immersing, for one minute, in a developer which comprised 12 parts by weight of benzyl alcohol, 5 parts by weight of sodium iso propyl naphthalenesulfonate, one part by weight of triethanolamine and 82 parts by weight of water and then rubbed with a developing pad to remove the light-sensitive layer and the silicone rubber layer on the non-exposed areas to thus give a lithographic printing plate requiring no dampening water.

The suitability for plate scanner of the resulting printing plate was determined. The results thus obtained are listed in Table 1 below.

## Comparative Example 2

To an aluminum substrate prepared in the same manner used in Comparative Example 1, there were applied, in order, a primer layer, a light-sensitive layer and a silicone rubber layer and the resulting original PS plate requiring no dampening water was imagewise exposed to light and developed in the same manner

used in Example 2 to give a lithographic printing plate requiring no dampening water.

The suitability for plate scanner of the resulting printing plate was determined. The results thus obtained are listed in Table 1 below.

Table 1: Results of Evaluation of Suitability for Plate Scanner

Ex. No.	1	1 *	2	2 *
Suitability for Plate Scanner	○	×	○	×
50% Area Ratio of half-tone dots * <sup>1</sup>				
perpendicular to rolling direction* <sup>2</sup>	52%	80%	51%	75%
parallel to rolling direction * <sup>3</sup>	50%	51%	50%	50%
specular gloss rate * <sup>4</sup> (%)	80	50	80	50
surface roughness ( $\mu$ m)	0.04	0.2	0.04	0.2

○ : good;                      × : not good

\*: Comparative Example

\*1: 50% area ratio of half-tone dots

This is a value obtained by imagewise exposing a PS plate to light through an original having a rate of area occupied by half-tone dots of 50% at a density of 133 lines/inch and determining the rate of area on the plate occupied by the half-tone dots using a plate scanner (Demia 640; available from Dainippon Ink & Chemicals, Incorporated).

\*2: The rate of area occupied by the half-tone dots observed when the lithographic printing plate was put on a printing press in such a manner that the rolling direction of the aluminum substrate of the plate is perpendicular to the direction of the vector component, parallel to the substrate surface, of the incident light from the light source of the plate scanner.

\*3: The rate of area occupied by the half-tone dots observed when the lithographic printing plate was put on a printing press in such a manner that the rolling direction of the aluminum substrate of the plate is parallel to the direction of the vector component, parallel to the substrate surface, of the incident light from the light source of the plate scanner.

\*4:      Rate of Specular Gloss(%) = (S.G.)<sub>v</sub> × 100/(S.G.)<sub>p</sub>

          (S.G.)<sub>v</sub> : specular gloss determined by making light  
                                incident upon the surface vertically to the  
                                rolling direction.

          (S.G.)<sub>p</sub> : specular gloss determined by making light  
                                incident upon the surface parallel to the  
                                rolling direction.

## Claims

1. A substrate for lithographic printing plate comprising a rolled aluminum plate whose specular gloss determined by making light incident upon the aluminum plate perpendicularly to the rolling direction of the rolled plate is at least 70% of that determined by making light incident upon the rolled plate parallel to the rolling direction of the rolled plate.
2. The substrate of claim 1 wherein the surface roughness of the rolling roll is not more than  $0.1\text{ }\mu\text{m}$  expressed in terms of central line average surface roughness:  $R_a$ .
3. The substrate of claim 2 wherein the surface roughness of the rolling roll is not more than  $0.05\text{ }\mu\text{m}$  expressed in terms of central line average surface roughness:  $R_a$ .
4. The substrate of claim 2 wherein the surface roughness of the aluminum substrate ranges from  $0.1$  to  $0.01\text{ }\mu\text{m}$  expressed in terms of central line average surface roughness:  $R_a$ .
5. The substrate of claim 1 wherein the aluminum plate comprises pure aluminum or an aluminum alloy having a foreign atom content of not more than 10% by weight.
6. The substrate of claim 1 wherein the thickness of the aluminum plate ranges from  $0.1$  to  $0.5\text{ mm}$ .
7. The substrate of claim 1 wherein after rolling the aluminum plate, it is degreased with an alkali under conditions of a concentration ranging from 1 to 50%, a temperature ranging from  $30$  to  $100^\circ\text{C}$  and a treating time ranging from 1 to 100 seconds.
8. The substrate of claim 7 wherein the aluminum plate is grained, after the degreasing treatment, under conditions of an electrolyte concentration ranging from 1 to 30% by weight, a temperature ranging from  $20$  to  $50^\circ\text{C}$ , a treating time ranging from 5 to 100 seconds and a current density ranging from 5 to  $100\text{ A/dm}^2$ .

9. The substrate of claim 8 wherein the aluminum plate is further hydrophilized under conditions of a concentration of treating solution ranging from 1 to 20% by weight, a temperature ranging from 20 to 80 ° C and a treating time ranging from 5 to 30 seconds.

5 10. The substrate of claim 1 wherein the lithographic printing plate is a lithographic printing plate requiring no dampening water.

11. The substrate of claim 1 wherein the lithographic printing plate is a lithographic printing plate prepared by an electrophotographic plate making process.

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European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

**EP 91 11 3068**

### 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)
A	WO-A-8 102 547 (FOLIENWALZWERK BRUEDER TEICH AKTIENGESELLSCHAFT) * claims 1-4 ** -- --	1	B 41 N 1/08 B 41 N 3/04 B 21 B 1/22
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 161 (P-702)(3008) 17 May 1988 & JP-A-62 275 267 ( KONISHIROKU PHOTO IND CO LTD ) 30 November 1987 * abstract ** -- --	1	
A	EP-A-0 098 166 (KONISHIROKU PHOTO IND CO LTD) * abstract *** page 3, line 13 - line 26 ** -- --	1	
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 287 (M-264)(1432) 21 December 1983 & JP-A-58 160 196 ( KAWASAKI SEITETSU K.K. ) * abstract ** -- --	1	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 78 (M-675)(2925) 11 March 1988 & JP-A-62 218 189 ( KOBE STEEL LTD ) 25 September 1987 * abstract ** -- --	1	
A	EP-A-0 257 957 (FUJI PHOTO FILM CO., LTD.) * abstract *** page 4, line 15 - page 5, line 45 ** -- -- -- --	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		08 October 91	MARKHAM R.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone		E : earlier patent document, but published on, or after the filing date	
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