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(54) Support for lithographic printing plate.

(57) Disclosed is a support for lithographic printing plate, comprising an electrodeposited chromium layer having protuberant portions on an iron material with a center line average roughness (Ra) of 0.1 to 3 μm.

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Support for lithographic printing plate

This invention relates to a support for lithographic printing plate, more particularly to a support for lithographic printing plate having an electrodeposited chromium layer on an iron material with its surface being roughened.

It has been known in the art to use iron materials with the surfaces roughened such as iron foils produced by the electrocasting method as the support for lithographic printing plate, as disclosed in Japanese Unexamined Patent Pulications Nos. 130395/1981, 130396/1981, 150592/1981 and 64597/1982.

However, the lithographic printing plates using these supports suffer from the drawback that a part of the image line portion may be peeled off during printing over a long term, thus being insufficient in printing life. There is also involved the problem that, in developing, the image line portion may be damaged by the so-called "hand development" in which developing is performed by rubbing the plate with a sponge impregnated with a developer without use of an automatic developing machine, namely the problem of narrow tolerance in developing methods.

Accordingly, it is an object of this invention to provide a support suitable for lithographic printing plate having sufficient performance in tolerance in developing methods and printing life.

Other objects of this invention will be apparent from the disclosure in this specification.

The objects of this invention can be accomplished by providing a support for lithographic printing plate, comprising an electrodeposited chromium layer having protuberent portions on an iron material with a center line average roughness (Ra) of 0.1 to 3 µm.

This invention will be described below in detail with reference to the accompanying drawings:.

In the drawings;

Fig. 1 is a scanning electron microscope photograph of the surface of an iron material with roughened surface before provision of an electrodeposited chromium layer (magnification : x 4,000, slanted angle: 30°); and Figs. 2 through 4 are scanning electron microscope photographs of the surface of the support of this invention (magnifications: x 4,000 in Fig. 2 and Fig. 3, x 3,000 in Fig. 4; slanted angle: 0° in Fig. 2, and 30° in any of others)

The iron material to be used in this invention is inclusive of pure iron and also alloys of iron with other elements. As other elements forming alloys with iron, there may be included carbon, manganese, nickel, and others.

Typical examples of alloys may include carbon steels (alloys of carbon (0.04 to 1.7 %) and iron), cast irons with higher contents of carbon than carbon steels, and further special steels (e.g. manganese steel, nickel steel, chromium steel, nickel-chromium steel) having added other elements (e.g. manganese, nickel, chromium, cobalt, tungsten, molybdenum), etc. The above carbon steels may include super-soft steels (0.25 % or less carbon), soft steels (0.25 to 0.5 % carbon), hard steels (0.5 to 1.0 % carbon) and super-hard steels (1.0 % or more carbon).

As the iron material of this invention, there may be employed plates (inclusive of foil-shaped ones) prepared by rolling, electrocasting, etc.

The iron material in this invention has its center line average roughness (Ra) of 0.1 to 3 µm. The center line average roughness (Ra) herein mentioned is the average of the absolute values of the deviations of the respective points on a roughness curve from the center line in a roughness profile as shown in DIN 4768, and it is represented in terms of the Ra value expressed in micron units, which value is determined by the formula shown below for a measured length of ℓ_m when the center line in the lateral direction is made X axis and that in the longitudinal direction Y axis, and the point on the roughness curve is represented by (x, y):

Formula:

$$Ra = 1/_{\ell m} \int_{0}^{\ell m} | y | dx$$

The Ra of the iron material of this invention is preferably 0.3 to 2 µm, particularly preferably 0.3 to 1.5 µm in view of water retentivity.

As the method for producing an iron material with such center line average roughness, there may be employed various methods known in the art, including, for example, the mechanical method, the chemical method and the electrolytic method. As the mechanical method, there may be included the ball graining method, the brush graining method and the graining method with liquid horning. As the chemical method, there may be included the methods of etching with solutions containing sulfuric acid, phosphoric acid, nitric acid, hydrochloric acid, oxalic acid, pyrophosphoric acid, ferric chloride, hydrogen peroxide, etc. As the electrolytic method, there may be included etching by electrolysis and plating by electrolysis. As the method of etching by electrolysis, there may be included the methods to carry out etching with the use of solutions containing phosphoric acid, sulfuric acid, perchloric acid, hydrochloric acid, nitric acid, pyrophosphoric acid, hydrofluoric acid, acetic anhydride, etc. As the method of plating by electrolysis, there may be included the methods in which an acidic bath such as sulfate bath, chloride bath, borofluoride bath, mixed salt bath (e.g. sulfate-chloride bath), ferrous sulfamate, etc is used. In preparation of the iron material roughened on its surface, various methods as mentioned above may be suitably chosen and employed depending on the composition of the iron material, etc. In this invention, the method of plating by electrolysis is particularly preferred.

The iron material in this invention has Ra of 0.1 to 3 µm, particularly preferably with a valley-count T_2 of 300 to 1500 at the cutting line at 0.4 µm as measured by the perthometer Type S5P produced by Perthen Co. The T_2 herein mentioned is a number of peaks per one inch which exceed the cutting line preset in the roughness profile R and thereafter valley goes below the center line.

The iron material with the roughened surface as described above may be applied with a surface treatment prior to provision of the electrodeposited chromium layer having projections, so long as the Ra value is maintained within the aforesaid range. As said surface treatment, there may be employed for example the plating in which zinc, nickel, copper, tin, chromium, etc. are plated by electroplating, chemical plating, hot dipping, gas-phase plating, etc. or the treatment or electrolysis with a phosphate, oxalate, chromate, etc.

When the iron material with roughened surface is thin as in case of a foil produced by the electrocasting method, a metal plate, a plastic film, etc. may be laminated directly or through an intermediary adhesive layer on the back surface thereof. This laminating step may be performed either before or after the step of providing the electrodeposited chromium layer having protrusions.

The iron material with roughened surface having applied the aforesaid surface treatment thereon or laminated with a metal plate, etc. on its back surface is also included within the iron material of this invention.

Next, the electrodeposited chromium layer having protrusions in the support for lithographic printing plate of this invention is to be explained.

As the electrodeposited chromium layer, there may be employed various kinds so long as Ra of the support for lithographic printing plate can be maintained within the range as specified above.

As the shape of the protrusions on the electrodeposited layer, preferable ones are, for example, those of coalescively agglomerated assemblages of subagglomerated spheroidate partricles of generally lobular curvilinear contour absent of angles, as disclosed in European Patent Publication No. 20021; and also those having crystalline products with angles and/or an agglomerated product thereof as disclosed in Japanese Patent Application No.

105724/1982 (corresponding to European Application No. 83303514.0. In particular, the electrodeposited chromium layer having crystalline products with angles and/or an agglomerated product thereof is more excellent in printing life, tolerance in developing methods, and preferred. As the crystalline products with angles are preferably in the shape of plates or hexahedrons such as cubes. As the plate crystals are preferred polygonal, primarily hexagonal, plates, and the polygonal shape may have sizes of faces preferably of 0.5 to 5 μm and thickness preferably of 0.01 to 0.8 μm. As the hexahedral crystals, cubic crystals, especially those having side length of 0.1 to 2 μm are preferred. The protrusions as described above may have a projected area percentage preferably of 20% or more. The projected area percentage herein mentioned refers to that obtained by projection in the direction perpendicular to the support face having the electrodeposited layer of this invention, namely orthographic projection, and said area percentage is measurable by means of microscopic photography, etc.

The protrusions may preferably be protrude on the surface of the electrodeposited chromium layer by 0.3 to 5 μm, particularly 0.5 to 4 μm.

The electrodeposited chromium layer may have a thickness preferably of 0.01 to 10 μm, particularly preferably 0.01 to 4 μm.

The thickness can be determined quantitatively as an average value by fluorescent X-ray analysis with reference to the calibration curve previously prepared from the standard chromium plated layer of known thicknesses.

The elemental composition of the electrodeposited chromium layer consists substantially of chromium and oxygen, and when analyzed from elemental analysis in the depth direction of the layer, it is observed as being constituted substantially of chromium oxides (hydrates are also included in these chromium oxides) and metallic chromium, the ratio of metallic chromium being increased as the depth is deeper. As the chromium oxides, there may be included oxides of divalent, trivalent and hexavalent chromium, primarily oxides of trivalent chromium.

Fig. 1 shows an electron microscope photograph of the surface of an iron material with roughened surface before provision of an electrodeposited chromium layer. Figs. 2 through 4 are electron microscope photographs of the surfaces of the supports according to this invention having electrodeposited chromium layers having protrusions on iron materials with roughened surfaces.

Next, typical methods for providing electrodeposited chromium layers having protrusions are shown.

An electrodeposited chromium layer having protrusions without protuberant angles, constituted of coalescively agglomerated assemblages of subagglomerated spheroidate partricles of generally lobular curvilinear contour absent of angles may be prepared by dipping an iron material into a grainer bath containing bifluoride and then applying an electroplating for at least 30 seconds in a plating bath containing water, anhydrous chromic acid and sulfuric acid in amounts which can maintain the ratio of Cr^{6+}/SO_4^{2-} at 75 to 180. Specific conditions are described in detail in European Patent Publication No. 20021.

As the preferable method for providing an electrodeposited chromium layer having protrusions which are crystalline products with angles and/or an agglomerated product thereof, for example, the Electrolyte 1 shown in Table 1 is cooled or heated to control its liquid temperature and electrolytic treatment is conducted under the Electrolysis Conditions 1 shown in Table 2. The Electrolyte 1 is a liquid for formation of the electrodeposited chromium layer of this invention on the surface of an iron material.

Table 1:	Electrolyte 1
Anhydrous chromic acid (Cr_2O_3)	100 - 500 g
Barium compound	1 - 10 g
Fluoride, e.g. hydrogen fluoride (HF)	0 - 20 g
Nitric acid	0 - 10 g
Acetic acid	0 - 1 g
make up to one liter with water	

Table 2:	Electrolysis Conditions 1
Direct current voltage	5 - 15 V
Current density	5 - 50 A/dm^2
Liquid temperature	0 - 60°C
Cathode	Iron material
Anode	Lead electrode
Area ratio of cathode to anode	1 : 1 to 1 : 1.5
Treatment time	2 - 6 min.

This method is described in detail in the specification aneexed to Japanese Patent Application No. 105724/1982 corresponding to European Application No. 83303514.0.

As another preferable method for providing an electrodeposited chromium layer having protrusions of crystalline products with angles and/or agglomerated products thereof, there may be mentioned the method in which electrodeposited coating is applied on an iron material in a placing liquid wherein $[Cr^{6+}]/[SO_4{}^{2-}]$ (where $[Cr^{6+}]$ representsan ion concentration of Cr^{6+} and

$[SO_4^{2-}]$ an ion concentration of SO_4^{2-}) is 75 to 180, at a current density of 100 A/dm^2 or less, at a temperature of 40°C or lower for 30 seconds or longer. In said plating liquid, $[Cr^{6+}]$ may preferably be 0.2 to 4.5 mol/lit., particularly preferably 0.5 to 3 mol/lit., while $[SO_4^{2-}]$ preferably 0.01 to 0.046 mol/lit., particularly preferably 0.015 to 0.03 mol/lit.. As the Cr^{6+} supplying source, anhydrous chromic acid is preferred, while as the SO_4^{2-} supplying source, sulfuric acid is preferred.

The ratio of the hexavalent chromium ion concentration to the sulfate ion concentration ($[Cr^{6+}]/[SO_4^{2-}]$) is 75 to 180, preferably within the range of from 80 to 130. The plating liquid may also contain fluorine compounds or strontium compounds, and others. As the fluorine compounds, there may be included ammonium fluoride, sodium silicofluoride, silicofluoric acid, chromium silicofluoride and the like. As the strontium compounds, there may be included strontium sulfate, strontium chromate, etc. A fluorine compound may be added in an amount of 0.5 to 10 g/lit., while a strontium compound in an amount of 3 to 20 g/lit.

According to the electrolysis conditions, the current density may be 100 A/dm^2 or less, preferably within the range from 10 to 30 A/dm^2. Further, the temperature of the plating bath may preferably 0 to 40°C, particularly preferably 10 to 30°C. The relation between the bath temperature and the current density may preferably be such that the current temperature may be higher when the bath temperature is higher, and the current temperature lower when the bath temperature is lower. Preferably, a combination of a bath temperature of 18 to 26°C and a current density of 15 to 20 A/dm^2 may be employed.

Before or after the treatment for providing an electrodeposited chromium layer (the main treatment), it is also possible to apply an appropriate pre-treatment or post-treatment.

As the pre-treatment method, there may be mentioned the following method. The Electrolyte 2 as shown in Table 3 and an iron plate as the counter-cathode are employed, and electrolytic treatment is carried out under the Electrolysis Conditions 2 as shown in Table 4.

Table 3: Electrolyte 2

Anhydrous chromic acid	80 - 200 g
Nitric acid (64 %)	0.5 - 1 ml
make up to one liter with water	

Table 4: Electrolysis Conditions 2

Direct current voltage	4 - 10 V
Current density	2 - 10 A/dm^2
Liquid temperature	10°C - 40°C
Anode	Iron material
Area ratio of cathode to anode	1 : 1
Treatment time	30 sec. - 5 min.

The thus pre-treated iron material is washed by showering with water and then transferred to the main treatment step.

As the preferable post-treatment method, the following method may be employed:

After the iron material having an electrodeposited chromium layer is optionally washed with an aqueous acid or alkali solution, it is subjected to the surface treatment with a surface treating solution of an aqueous permanganate solution.

As the preferable permanganate to be used in the above surface treating solution, there are lithium permanganate, sodium permanganate, potassium permanganate, rubidium permanganate, calcium permanganate, barium permanganate, etc. The concentration of a permanganate in the treating solution employed may preferably be 0.05 to 10 % by weight, particularly preferably 1 to 5 % by weight. The temperature of the treating solution may preferably be 0 to 80°C, particularly preferably 20 to 50°C.

Another preferable method for the post-treatment step is the following method.

After the iron material having an electrodeposited chromium layer is optionally washed with an aqueous acid or alkali solution, it is subjected to the surface treatment with a surface treating solution containing a water soluble polymeric compound and at least one selected from water soluble salts of calcium, magneisum, zinc, barium, strontium, cobalt, manganese, nickel and silicon.

The water soluble polymeric compounds may preferably those having solubilities of 0.01 % or higher. As preferable water soluble polymeric compounds, there may be included natural polymeric compounds such as gum arabic, starch, dextrin, sodium alginate, gelatin, etc.; water soluble cellulose compounds such as water soluble salts of carboxyalkyl cellulose (as alkyl, methyl, ethyl, propyl, etc.), alkyl celluloses as exemplified by methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and the like; synthetic polymeric compounds such as polyacrylic acid or water soluble salts thereof, polymethacrylic acid or water soluble salts thereof, acrylic acid copolymers or water soluble salts thereof, methacrylic acid copolymers or water soluble salts thereof, styrene-maleic anhydride copolymers, polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone, etc. The water soluble salts of these polymeric compounds may include sodium and potassium salts. The above various water soluble polymeric compounds may be used either singly or in combination of two or more kinds. Among the water soluble polymeric compounds, natural polymeric compounds such as starch, dextrin, etc. and water soluble cellulose compounds are preferred. These polymeric compounds may have molecular weights preferably of 500 to 1,000,000.

Water soluble salts to be used together with the water soluble polymeric compound are those having solubilities of 0.01 % or higher, particularly salts of inorganic or organic acids with calcium, magnesium, zinc, barium, strontium, cobalt, manganese, nickel and silicon. The salts may contain complex salts. Typical organic acid salts are those of carboxylic acids such as acetic acid, propionic acid, butyric acid, succinic acid, benzoic acid, salicylic acid and acetylacetone complex. Typical inorganic salts are chlorides, bromides, chlorates, bromates, iodides, iodates, nitrates, sulfates and phosphates. Water soluble salts may be used either singly or in combination of two or more kinds.

As the water soluble salt, an organic salt is particularly preferred, and the salts with calcium, magnesium, barium and zinc are particularly preferred. The amount of the layer containing the water soluble polymeric compound and the water soluble salt after dried is preferably of 0.001 to 1 mg/dm^2, particularly 0.05 to 0.5 mg/dm^2. This method and the skin film formed are described in further detail in the specification annexed to Japanese Patent Application No. 105726/1982 corresponding to European Application No. 83303513.2).

Photosensitive lithographic printing plates can be produced by coating photosensitive compositions, for example, with the use of organic solvents, on the support of this invention.

Photosensitive compositions contain as essential components photosensitive substances. As the photosensitive substance, there may be employed a substance which can be exposed to light to vary in solubility of the photosensitive composition layer relative to the developer, to vary in adhesive force between molecules before and after exposure or to vary in affinity f the layer for water and oil.

In the following, typical examples of such substances are described. First, there may be mentioned posi-type photosensitive substances of quinoneazide type such as o-naphthoquinonediazide compounds well known in the art.

o-Quinonediazide compounds are compounds having at least one o-quinonediazide group, preferably o-benzoquinodiazide group or o-naphthoquinonediazide group, and are inclusive of compounds of various known structures, as described in detail in J. Kosar "Light-Sensitive Systems" (published by John Wiley & Sons, Inc., 1965), pp. 339 - 353. In particular, esters of various hydroxyl compounds with o-naphthoquinonediazide sulfonic acid are preferred. As preferable hydroxyl compounds, there may be included condensed resins of phenols with carbonyl containing compounds, especially resins obtained by condensation in the presence of an acidic catalyst. Said phenols may include phenol, resorcin, cresol, pyrogallol and the like, while said carbonyl containing compounds may include aldehydes, such as formaldehyde, benzaldehyde, and ketones such as acetone. Particularly, phenol-formaldehyde resins, cresol-formaldehyde resins, pyrogallol-acetone resins and resorcin-benzaldehyde resins are preferred.

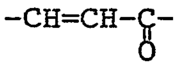
Typical examples of o-quinonediazide compounds may include esters of benzoquinond-(1,2)-diazidesulfonyl chloride or naphthoquinone-(1,2)-diazidesulfonyl chloride with phenol-formaldehyde resins; sulfonic acid esters of naphthoquinone-(1,2)-diazidesulfonyl chloride and pyrogallol-acetone resins as disclosed in U.S. Patent 3,635,709; condensed products of naphthoquinone-(1,2)-diazide-(2)-5-sulfonyl chloride and resorcin-benzaldehyde resins as disclosed in Japanese Unexamined Patent Publication No. 1044/1981; ester compounds of naphthoquinone-(1,2)-diazide-(2)-5-sulfonyl chloride and resorcin-pyrogalol-acetone co-condensed products as disclosed in Japanese Unexamined Patent Publication No.76346/1980; as other useful o-quinonediazide compounds, those obtained by the esterification reaction of o-naphthoquinonediazidesulfonyl chloride with polyesters having terminal hydroxyl groups as disclosed in Japanese Unexamined Patent Publication No. 117503/1975 and those obtained by the esterification reaction of o-naphthoquinonediazidesulfonyl chloride with p-hydroxylstyrene homopolymers or copolymers of p-hydroxylstyrene with other copolymerizable monomers; and so on.

These o-quinonediazide compounds may be contained preferably in amounts of 5 to 80 % by weight, particularly pareferably 10 to 50 % by weight, based on the total solids of the photosensitive composition.

Such a quinonediazide type posi-type photosensitive material may preferably be used in combination with an alkali-soluble resin as binder. As alkali-soluble resins are preferred those obtained by reacting phenols with ketones or aldehydes in the presence of an acidic catalyst. Said phenols may include, for example, phenol, cresol, p-substituted phenols and the like. Said aldehydes may include, for example, acetaldehyde, formaldehyde and the like, preferably formaldehyde. As ketones, acetone is preferred.

As preferable alkali-soluble resins, there may be included, for example, phenol-formaldehyde resins, cresol-formaldehyde resins, phenol-cresol-formaldehyde co-condensed resins as disclosed in Japanese Unexamined Patent Publication No.57841/ 1980, co-condensed resins of p-substituted phenol, phenol or cresol and formaldehyde as disclosed in Japanese Unexamined Patent Publication No.127553/1980, condensed products of polyhydric phenols with benzaldehyde such as resorcinbenzaldehyde resins, pyrogallol-benzaldehyde resins, etc., co-codensed products of polyhydric phenols with acetone such as pyrogallol-resorcin-acetone resin, etc., xylenol-formaldehyde resins and others. These alkali-soluble resins may be contained preferably in amounts of 30 to 90 % by weight, particularly 50 to 85 % by weight, based on the total solids in the photosensitive composition.

As other photosensitive substances, there may also be employed diazo resins, typically condensed products of aromatic diazonium salts and formaldehyde. Particularly preferably, there may be included salts of condensed products of p-diazodiphenylamine and formaldehyde or acetaldehyde, diazo resin inorganic salts which are the reaction products of hexafluorophosphates, tetrafluoroborates, perchlorates or periodates with said condensed products, diazo resin organic salts of said condensed products with sulfonic acids as disclosed in U.S. Patent 3,300,309, and the like. Further, diazo resins may be used preferably together with binders. As such binders, there may be employed various polymeric compounds, preferably copolymers of monomers having aromatic hydroxyl groups such as N-(4-hydroxyphenyl)-acrylamide, N-(4-hydroxyphenyl)methacrylamide, o-, m-, or p-hydroxystyrene, o-, m- or p-hydroxyphenyl methacrylate, etc. with other monomers as disclosed in Japanese Unexamined Patent Publication No.98613/1979; polymers containing hydroxyethyl acrylate units or hydroxyethyl methacrylate units as primary recurring units as disclosed in U.S. Patent 4,123,276; natural resins such as shellac, rosin, etc.; polyvinyl alcohol; polyamide resins as disclosed in U.S. Patent 3,751,257; linear polyurethane resins as disclosed in U.S. Patent 3,660,097; phthalated resins of polyvinyl alcohol; epoxy resins condensed from bisphenol A and epichlorohydrin; celluloses such as cellulose acetate, cellulose acetate phthalate and the like.

As still other photosensitive substances, there may suitably be employed those containing as principal components photosensitive polymers such as polyesters, polyamides or polycarbonates including  $-CH=CH-\underset{\underset{O}{\|}}{C}-$ as photosensitive groups in the polymeric main chain or side chain. For example, there may be included photosensitive polyesters obtained by condensation of phenylenediethyl acrylate, hydrogenated bisphenol A and triethyleneglycol as disclosed in Japanese Unexamined Patent Publication No. 40415/1980; photosensitive polyester compounds derived from (2-propenylidene)malonic acid compounds such as cinnamilidene malonic acid and bifunctional glycols as disclosed in U.S. Patent No. 2,956,878; and so on.

Further, as still other photosensitive substances, there may also be used aromatic azide compounds having azide groups directly or through carbonyl group or sulfonyl group bonded to aromatic rings. For example, there may be included polyazidestyrene, polyvinyl-p-azidebenzoate, polyvinyl-p-azidebenzal as disclosed in U.S. Patent 3,096,311; the reaction products of azidearylsulfanyl chloride and unsaturated hydrocarbon type polymers as disclosed in Japanese Patent Publication No.9613/1970; and polymers having sulfonylazide or carbonylazide as disclosd in Japanese Patent Publication Nos. 21067/1968, 229/1969, 22954/1969 and 24915/1970. As still another photosensitive substance, there may also be employed a photopolymerizable composition comprising an addition polymerizable unsaturated compound.

The support of this invention can be used as a support of a lithographic printing plate obtained by electrophotographic process.

Representative methods forming a printing plate by electrophotography are shown below:

(1) A method comprising; forming a toner-image by electrophotography on a lithographic printing plate material comprising a support of this invention having a photoconductive layer thereon, and making hydrophilic the surface of the photoconductive layer at non-image portion.

(2) A method comprising; forming a toner-image by electrophotography on a lithographic printing plate material comprising a support of this invention having a photoconductive layer thereon, and removing the photoconductive layer at non-image portion.

(3) A method comprising; transferring a toner-image formed by electrophotography onto a lithographic printing plate material comprising a support of this invention having a polymeric layer thereon, fixing the toner-image transferred by heating, and removing the polymeric layer at non-image portion.

The lithographic printing plate obtained by the method (1) comprises a support of this invention having a photoconductive layer on the total surface thereof and having a toner-image only at image portion on said photoconductive layer.

The lithographic printing plate obtained by the method (2) comprises a support of this invention having a photoconductive layer only at an image portion thereon and having a toner-image on the entire surface of said photoconductive layer.

The lithographic printing plate obtained by the method (3) comprises a support of this invention having a polymeric layer only at an image portion thereon and having a toner-image on the total surface of said polymeric layer.

The photoconductive layer mentioned above comprises a photoconductive material. The photoconductive material may be, for example, an inorganic or organic photoconductive material or a photoconductive organic pigment. At least one of them is used. The inorganic photoconductive material may be, for example, selenium- or zinc oxide-based material, cadmium sulfide or the like which are known for electrophotography. The organic photoconductive material may be, e.g. polyvinylcarbazole, oxazoles or pyrylium salt. Examples of the photoconductive organic pigments are phthalocyanine, quinacridone pigments or the like.

It is possible to use in said photoconductive layer such sensitizing dyes or chemical sensitizing agents as described in Japanese Patent Publication No. 7333/1965 and Japanese Unexamined Patent Publication No. 134632/1979. The aforesaid photoconductive material (and sensitizing agent) can be dissolved or suspended in a solution containing at least one natural or synthetic high-molecular substance (e.g. styrene, silicone or phenol resin or the like), coated onto a support and dried according to a known procedure. The photoconductive layer may also contain various additives, for example, surface active agents for improving the coating property, and plasticizers for imparting softness and wear resistance to the coated layer. It is also possible to form an intermediate layer (e.g. of polyvinyl alcohol, ethyl cellulose, polyacrylic acid or the like) between a support and the photoconductive layer so as to improve the electrophotographic characteristics.

The thickness of the photoconductive layer after drying is preferably 1 μ to 50 μ, and more preferably 1 μ to 15 μ.

The thus obtained printing plate material is then electrostatically charged by the usual electrophotography, and exposed to the xenone, halogen, fluorescent, or tungsten-filament lamp or to a laser beam such as semiconductor, Ar^+ or He-Ne laser, thereby to form an electrostatic latent image. The formed latent image is then toner-developed.

In the above-mentioned method (1) or (2), wherein the support of this invention is used as a support for said photoconductive layer, the toner-image is, after toner-developing, fixed with heat by use of a heat plate, heat roller, heat rays or the like. Then, in the non-imaged area (where there is no toner attached), the photoconductive layer is made hydrophilic in the method (1) or removed by use of an appropriate solvent in the method (2) to give a lithographic printing plate.

In the above mentioned method (3), it is not essential to use a support of this invention as a support of a photoconductive layer. After toner-developing, the toner-image is transferred onto a polymeric layer which a support of this invention has thereon and the transferred toner-image is fixed with heat. Then the polymeric layer in the non-imaged area is removed to give a lithographic printing plate.

For the toner development, it is possible to use a dry process in which both toner and carrier are solid, a wet process in which the toner or the carrier is liquid, or an aerosol process in which a gas flow is used as the carrier regardless of whether the toner is solid or liquid.

It is preferable that the toner is hydrophobic and has an ink accepting property. The toner may have positive or negative polarity,

With the lithographic printing plate material mentioned above, it is possible to obtain both positive-positive and negative-negative printing plates with only one toner developer by use of the charging property to both positive and negative polarities.

The support of this invention can be used as a support of lithographic printing plate obtained by the use of a silver halide emulsion.

Representative methods using a silver halide emulsion are shown below:

(1) A method comprising; exposing a lithographic printing plate material comprising a support of this invention having a silver halide emulsion layer thereon and having a tanning developing agent such as polyhydroxybenzene in said emulsion layer or a separate layer, and tanning developing agent with an alkaline solution. In the printing plate obtained by this method, the developed area has an ink accepting property. It is preferable that the layer in a non-developed area is removed with warm water and the like. This method is descrived in detail, for example, in United States Patent Nos. 3146104 and (T)

881005, and Japanese Patent Publication No. 23166/1970.

(2) A method comprising; exposing a silver halide emulsion layer, developing the exposed silver halide emulsion in the presence of a silver halide solvent, transferring the silver complex produced on said development into a layer (preferably a separate layer from the emulsion layer) containing physical development nuclei, and forming an image portion by physical development.

In this method, a support of this invention is used as a support of a physical development nuclei-containing layer. This silver halide emulsion layer may be carried on the support having the physical development nuclei layer or a separate support. The silver complex may be produced in an exposed area or non-exposed area. A method producing in non-exposed area is described in detail in, for example, United States Patent Nos. 3083097 and 3161508, Japanese Patent Publication Nos. 26526/1971, 16725/1973, and 30562/1973.

The method producing a silver complex in an exposed area comprises exposing an element comprising a support carrying silver halide particles, non-photosensitive metal salt particles being more soluble than the silver halide particles and the surface portion thereof being made less soluble and physical development nuclei, and treating the exposed element with a treating solution containing a material capable of solving said metal salt particles, and is described in detail, for example, in Japanese Unexamined Patent Publication Nos. 48554/1979, 165140/1981, 44138/1982 and 44153/1982.

(3) A method being so-called etching bleach process described in detail in, for example, United States

Patent No. 3385701. Belgian Patent No. 717466, British Patent No. 1235911, and Japanese Patent Publication No. 27242/1969.

The support of this invention can be used as a support of a lithographic printing plate requiring no damping water. The lithographic printing plate material giving the printing plate comprises a support of this invention having a ink-repelling layer thereon.

In case the ink-repelling layer becomes reactive on light exposure, it does not require other layer than the ink-repelling layer. In case the ink-repelling layer does not become reactive on light exposure, it requires a lightsensitive layer other than the ink-repelling layer.

Representative printing plate materials are shown below:

(1) A lithographic printing plate material comprising a support of this invention having as an essential layer a ink-repelling layer being reactive on light exposure thereon.

(2) A lithographic printing plate material comprising a support of this invention having as essential layers a layer containing a photosensitive substance and an ink-repelling layer in this order.

A usable photosensitive substance may be any known one for such a printing plate, e.g., a diazonium salt such as formaldehyde condensate of p-diazodiphenylamine salt, an o-naphthoquinonediazide compound, a photopolymerizable photosensitive material having an ethylenically unsaturated group, an azide compound, an α,β-unsaturated ketone compound, an α-phenylmaleimide compound and the like, a compound obtained by reacting the above-listed photosensitive materials and silicone compounds, or the like.

The aforesaid ink-repelling layer may be formed by use of diorganopolysiloxane compounds such as dimethylpolysiloxane and diphenylpolysiloxane, copolymers of these compounds, poly-fluorinated compounds, or the like.

The ink-repelling layer which becomes reactive on light exposure may be formed by use of organopolysiloxane, poly-fluorinated compound, or the like each having a photosensitive group.

The lithographic printing plate material described above is exposed through a positive or nagative film to an active light beam emitted from a mercury vapor, a carbon arc, a metal halide lamp or the like. The exposed printing plate material is then developed with a developing solution suitable for the photosensitive substance to complete the printing plate. The thus obtained printing plate is then used for printing with a printing press which is not equipped with damping water feeder.

The support of this invention can be used as a support of a duplicate plate obtained by such a method that comprises printing on a support of a duplicate plate from an original printing plate by use of a material such as an ink which can be hardened and becomes ink-receptive after hardening the material on the support of the duplicate plate.

The method is described in detail in Japanese Unexamined Patent Publication Nos. 46973/1980, 100005/1978, etc.

The support of this invention has a complicated surface shape, in which there exist fine grain surface of an electrodeposited chromium layer having protrusions in rough grain surface of an iron material, as shown in Fig. 2 through 4, and therefore, when provided for use in the photosensitive lithogaphic printing plate, it is excellent in adhesion to the layer having a number of polymeric compounds having a lipophilic layer such a photosensitive layer to be provided thereon, to give good printing life. Also, due to broad tolerance in developing methods, the image portion will very rarely be lost even by the "hand developoment" which is a treatment with a developer with more frictions than necessary.

Further, due to its surface shape, the support of this invention is good in water retentivity during printing, whereby management of water can easily be done and it is also very difficultly troubled by scamming. Also, the durability of the image line portion to the treating chemicals employed during printing, etc. is also good.

The present invention is illustrated in further detail by referring to the following Examples, by which the embodiments of the present invention are not limited.

Example 1

On a steel plate with a thickness of 0.1 mm, there was applied iron plating to a thickness of 5 µm, using a carbon plate as the anode and an electrolyte of pH 0.8 containing 400 g/lit. of ferrous chloride and 200 g/lit. of calcium chloride under the conditions of a bath temperatue of 100°C and a current density of 30 A/dm_2, to obtain an iron plated steel plate having a center line average roughness Ra on the surface of 0.5 µm.

The iron plated steel plate was applied with chromium plating, using an electrolyte containing 250 g/lit. of anhydrous chromic acid and 2.5 g/lit. of sulfuric acid under the conditions of a bath temperature of 20°C, a current density of 20 A/cm^2 and an electrolysis time of one minute.

The steel plate having thus been subjected to the main treatment step was then washed by showering with water and transferred to the subsequent post-treatment step. In the post-treatment step, the plate was first dipped in an aqueous 5 % caustic soda solution at 40°C for one minute, followed by washing by showering with water, and then dipped in an aqueous solution of carboxymethyl cellulose sodium salt and calcium acetate (each 0.07 wt.%) at room temperature for about one minute, followed by washing by showering with water. After completion of the post-treatment step, the treated plate was dried on cool air.

Next, on this support was coated a photosensitive coating solution having the following composition by a rotary coating machine, followed by drying at 100°C for 4 minutes, to obtain a lithographic printing plate material.

[Photosensitive coating solution composition]

Esterified product of naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid chloride with m-cresol-formaldehyde novolak resin (condensation degree: 25 mol %)	.... 3.5 g
m-Cresol-formaldehyde novolak resin	.... 8.0 g
Naphthoquinone-(1,2)-diazide-(2)-4-sulfonic acid chloride	.... 0.15 g
Esterified product of p-octylphenol-formaldehyde novolak resin and naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid chloride (condensation degree: 50 mol %)	.... 0.12 g

Oil blue #603 (produced by Orient Kagaku Co., Ltd.)..0.2 g

Ethyl cellosolve .... 100 g

The weight of the coating after drying was about 2.7 g/m^2.

On the thus obtained lithographic printing plate material were closely contacted a posi-manuscript film and the Step Tablet for measurement of sensitivity (produced by Eastman Kodak Co., No.2, 21 steps with density differences each of 0.15), and light exposure was applied by a 2 KW metal halide lamp (Idolfin 2000 produced by Iwasaki Denki Co., Ltd.) as the light source from a distance of 1 m for 80 seconds, followed by development with an aqueous 4 % sodium metasilicate solution at 25°C for 45 seconds to obtain a lithographic printing plate.

For examination of the adhesion between the support and the image line portions and the printing life of the printing plate, treating chemicals resistance test and printing test were conducted. As the treating chemicals resistance test, durability to aqueous isopropyl alcohol solution used in Darlgrain damping water system was examined.

The printing plate having formed an image with density differences on the steps of the above gray scale was immersed in an aqueous 35 % isopropyl alcohol solution at room temperature for 10 minutes and washed with water, and then the image portion was rubbed with a defatted cotton impregnated with water. By comparison of the resultant image portion with the image portion before immersing in isopropyl alcohol, the extent of corrosion to the chemicals of the image portion was judged. As the result, the aforesaid printing plate was free from corrosion to exhibit good resistance to the treating chemicals.

Printing life test was conducted by carrying out printing with the printing plate mounted on an offset printing machine (Hamadastar 900 CDX), and evaluated by the number of printed sheets obtained until there are formed damages on the image portion to make printing no longer possible. As the result, with the use of the aforesaid printing plate, good printing products were obtained up to 220,000 sheets. The above printing plate was also difficultly troubled by scamming during printing and had excellent water retentivity.

Example 2

The iron plated steel plate applied with iron plating under the same conditions as in Example 1 was applied with the electrolyte having the following composition under the electrolysis conditions shown below.

Electrolyte

Anhydrous chromic acid	430 g/lit.
Barium nitrate	3.8 g/lit.
Nitric acid (64 %)	1.2 ml/lit.
Amonium hydrogen fluoride	5 g/lit.
Acetic acid	0.2 g/lit.
Barium fluoride	0.1 g/lit.

Electrolysis Conditions

Current density	5 A/dm^2
Liquid temperature	5^{o}C
Cathode	Iron plated steel plate
Anode	Lead plate
Treatment time	5 min.

Then, the post-treatment was applied similarly as in Example 1, followed by washing with water and drying.

On the steel plate support having an electrodeposited chromium layer on its surface thus obtained, the coating with the same recipe as employed in Example 1 was applied similarly to obtain a lithographic printing plate material.

Such a lithographic printing plate material was subjected to exposure and developing in the same manner as in Example 1 to obtain a lithographic printing plate, which was in turn tested for the same treating chemicals resistance and printing life as in Example 1. As the result, this printing plate was found to be excellent in treating chemicals resistance, water retentivity and printing life, similarly as in Example 1, and good printed products up to 250,000 sheets were obtained.

Comparative Example 1

On the iron plated steel plate applied with iron plating under the same conditions as in Example 1, there was applied chromium plating to a thickness of 0.1 µm, using an electrolyte containing 250 g/lit. of anhydrous chromic acid and 2.5 g/lit. of sulfuric acid under the conditions of a bath temperature of 45°C and a current density of 40 A/dm^2. The surface of the support having an electrodeposited chromium layer on its surface thus obtained was confirmed by electron microscope photograph to be flat without protrusion of crystalline products.

Next, the same post-treatment as in Example 1 was conducted, followed by washing with water and drying. Then, the coating with the same recipe as employed in Example 1 was applied similarly to obtain a lithographic printing plate material.

Such a lithographic printing plate material was subjected to exposure and developing in the same manner as in Example 1 to obtain a lithographic printing plate, which was in turn tested for the same treating chemicals resistance and printing life as in Example 1. As the result, this printing plate was found to be poor in treating chemicals resistance with corrosion of image portion markedly recognized, and printing life was also poor, with a damage of the image portion being generated on printing of 90,000 sheets.

Example 3

The same kind of the steel plate as employed in Example 1 was applied with the same main treatment and the post-treatment as in Example 1.

Next, on this iron plate was coated a photosensitive coating solution having the following composition, followed by drying at 100°C for 4 minutes, to provide a lithographic printing plate material.

[Composition of photosensitive coating solution]

Condensed product of naphthoquinone-(1,2)-diazide-(2)-5-sulfonic acid chloride and resorcin-benzaldehyde resin (synthesized according to the method as described in Example 1 in Japanese Unexamined Patent Publication No.1044/1981)	.... 3.5 g
Co-condensed resin of phenol, m-, p-cresol mixture and formaldehyde (molar ratio of phenol to cresol: 3 : 7, weight average molecular weight: 1500)	.... 8 g
Naphthoquinone-(1,2)-diazide-(2)-4-sulfonic acid chloride	...... 0.15 g
Oil Blue #603 (produced by Orient Kagaku Kogyo Co.,Ltd.)	...... 0.2 g
p-t-Butyl phenol - formaldehyde novolak resin	..... 0.15 g
Methyl cellosolve	.... 100 g

The weight of the coating after drying was about 2.5 g/m^2.

On the thus obtained lithographic printing plate material were closely contacted Step Tablet for measurement of sensitivity (produced by Eastman Kodak Co., No.2, 21 steps with density differences each of 0.15) and a posi manuscript film, and light exposure was applied by a 2 KW metal halide lamp (Idolfin 2000 produced by Iwasaki Denki Co., Ltd.) as the light source from a distance of 1 m for 80 seconds, followed by development with an aqueous 4 % sodium metasilicate at 25°C for 45 seconds to obtain a lithographic printing plate.

For examination of the adhesion between the support and the image line portions and the printing life of the printing plate, treating chemicals resistance test and printing test were conducted. As the treating chemicals resistance test, was examined the durability to Ultra-plate Cleaner (produced by A.B. Chemical Co.) which is used as the washing liquid for removal of the scumming generated at the non-image portion during printing.

The printing plate having formed an image with density differences on the steps of the above gray scale was immersed in the stock solution of Ultra Plate Cleaner at room temperature for 20 minutes and washed with water. By comparison of the resultant image portion with the image portion before immersion, the extent of corrosion to the chemical of the image portion was judged. As the result, the aforesaid printing plate was free from corrosion and also, with respect to the dots, the dots of an area percentage of 2 % were maintained, thus exhibiting good resistance to the treating chemicals. Printing life test was conducted similarly as in Example 1. As the result, with the use of the aforesaid printing plate, good printing products were obtained up to 250,000 sheets. This printing plate had good water retentivity and printing could easily be managed.

Example 4

The same kind of the steel plate as employed in Example 1 was applied with the iron plating and the chromium plating similarly as in Example 2, followed by washing with water and drying.

Next, on this support was coated a photosensitive coating solution having the composition shown below by use of a rotary coating machine, followed by drying at 85°C for 3 minutes, to obtain a lithographic printing plate material.

[Photosensitive coating composition]

Copolymer A	5.0 g
Diazo resin B	0.5 g
Jurymer-AC-10L (produced by Nippon Junyaku Co.)	0.05 g
Aizen Victoria Pure Blue (produced by Hodogaya Kagaku Co.)	0.1 g
Methyl cellosolve	100 ml

The above copolymer A was obtained by dissolving a composition in terms of molar ratio of p-hydroxyphenyl methacrylamide/acrylonitrile/ethyl acrylate/methacrylic acid = 10/30/60/6 and 1/400 mole of azobisisobutyronitrile to the above monomers in methyl cellosolve, heating the solution in a sealed tube replaced with nitrogen at 65°C for 10 hours, and after completion of the reaction pouring the reaction mixture into water under stirring, followed by filtration and drying of the white precipitates formed. The diazo resin B is a hexafluorophosphoric acid salt obtained by mixing an aqueous 5 % diazo resin (trade name: D-012 produced by E.H.C. Co.) and an aqueous 10 % ammonium hexafluorophosphate, recovering the precipitates formed by suction filtration and drying the precipitates under reduced pressure at 30 to 40°C. The above copolymer had a weight average molecular weight of 80,000, and further the molecular weight distribution of the above resin was measured by gel permeation chromatography (GPC) to find that the fractions with molecular weights of trimer or lower comprise 93 % of the total fractions.

The weight of the coating after drying was 2.0 g/m^2.

On the thus obtained lithographic printing plate material was closely contacted a nega-manuscript film and light exposure was applied thereon at a distance of 1 m from a 2 KW metal halide lamp (Idolfin 2000, produced by Iwasaki Denki Co.,Ltd.) as the light source, followed by development with a developer having the following composition, to obtain a lithographic printing plate.

[Composition of developer]

Phenyl cellosolve	100 g
Diethanolamine	50 g
Pionin A-44B(produced by Takemono Yushi Co.,Ltd.)	30 g
Water	780 g

The developing conditions were 25°C and 45 seconds.

For examination of the adhesion between the support and the image portion, tolerance of developing methods and printing life of the printing plate, "hand developing" treatment, the treatment by means of an automatic developing machine and printing test were conducted.

Hand developing was carried out by impregnating a sponge sufficiently with the above developer, rubbing uniformly and lightly the surface of the above lithographic printing plate material having finished exposure with the sponge for 2 minutes, followed by washing with water. As the result, the above lithographic printing plate material was not damaged at the image portion at all both by the hand developing and by the developing machine. Printing test was performed similarly as in Example 1. As the result, the lithographic printing plate using the support of this invention gave good printed products up to 220,000 sheets.

Comparative Example 2

The same kind of the steel plate employed in Example 1 was applied with the same iron plating and chromium plating as in Comparative Example 1.

Next, the photosensitive coating solution with the same composition as in Example 4 was applied on this support and dried to obtain a lithographic printing plate material. Then, following the same procedure as in Example 4, a lithographic printing plate was prepared and printing life test was conducted therefor. As the result, in hand developing treatment, the image line portion was markedly damaged until it was almost peeled off. Further, in printing, a part of the image line portion was peeled off on printing of 80,000 sheets and printing became no longer possible.

Example 5

The same kind steel plate as employed in Example 1 was applied with the same iron plating as in Example 1, then with zinc plating to a thickness of 1.4 µm, and then with the same chromium plating as in Example 1, following subsequently the procedure as in Example 1, to obtain a lithographic printing plate.

When this printing plate was employed to carry out printing similarly, there were obtained printed products of good quality without problems of scumming.

Example 6

The same kind steel plate as employed in Example 1 was applied with the same iron plating as in Example 1, then with nickel plating to a thickness of 2 μm, and then with the same chromium plating as in Example 1, following subsequently the procedure as in Example 1, to obtain a lithographic printing plate.

When this printing plate was employed to carry out printing similarly, there were obtained printed products of good quality without problems of scumming.

Example 7

The same kind of the steel plate as employed in Example 1 was sbujected to etching with a ferric chloride solution of Baume 40° to roughen the center line average roughness Ra on the surface to 0.7 μm.

Then, the same chromium plating as in Example 1 was applied on the treated plate, followed by the same procedure as in Example 1 to obtain a lithographic printing plate.

When this printing plate was employed to carry out printing similarly, there were obtained printed products of good quality without problems of scumming.

Example 8

The following composition was dispersed and homogenized in a ball mill at normal temperature for 48 hours:

Zinc oxide	95 parts by weight
Methylsilicone resin (50% solution in toluene)	80 parts by weight
Toluene	100 parts by weight
Ethyl alcohol	25 parts by weight

The obtained coating composition was applied onto the support used in Example 2 to a thickness of 10 µ after drying. The thus formed printing plate material was then negatively charged using corona discharge equipment, and exposed imagewise to a light source consisting of ten 20 W fluorescent lamps through a lens system by use of a reflection positive original. The electrostatic latent image thus formed was then toner-developed using a polystyrene-based toner and by the magnet brush process. The resulting toner image was then fixed with heat, and subjected to hydrophlicity-imparting treatment to form a printing palte. When used for printing with an offset press, this printing plate yielded 400,000 satisfactory prints having a sharp image.

Example 9

The iron plated steel plate applied with iron plating under the same conditions as in Example 1 was applied with the electrolyte having the following composition under the electrolysis conditions shown below:

Electrolyte

Anhydrous chromic acid	400 kg
Barium nitrate	3.8 kg
Nitric acid (64 %)	1.2 lit.
Amonium hydrogen fluoride	5 kg
Acetic acid	0.2 kg
Barium fluoride	0.1 kg
Water to make 1000 lit.	

Electrolysis Conditions

Current density	10 A/dm^2
Liquid temperature	30°C
Cathode	Iron plated steel plate (1.3 m^2)
Anode	Lead plate (1.2 m^2)
Treatment time	5 min.

Then, the post-treatment was applied similarly as in Example 1, followed by washing with water and drying.

The following composition was dispersed and homogenized in a ball mill at normal temperature for 48 hours:

Zinc oxide	1 part by weight
m-Cresol-formaldehyde-novolak resin	2 parts by weight
Rose Bengale	0.01 part by weight
Methyl ethyl ketone	1 part by weight

The obtained coating composition was applied onto the support to a thickness of 5 μ after drying. After being charged, exposed, toner-developed and fixed with heat as described in Example 8, this plate was dipped in an aqueous alkali solution containing sodium silicate and sodium hydroxide to dissolve and remove the photoconductive layer in the non-image area (where the toner is not attached). When used for printing with an offset press, the thus obtained printing plate yielded 400,000 satisfactory prints having a sharp image.

Example 10

ε-Type copper phthalocyanine	1 part by weight
m-Cresol phenol formaldehyde novolak resin	6 parts by weight
Ethylene glycol monoethyl ether	24 parts by weight

The above composition was dispersed with ultrasonic dispersing equipment at normal temperature for 5 minutes, and used to make a printing plate material as described in Example 9. The plate material was then treated in the same way as in Example 9 to form a printing plate. The printing life of this printing plate was 350,000 prints or more.

Example 11

The printing plate material obtained in Example 10 was positively charged using corona discharge equipment. An image was photographed at an enlarging factor of 16 (area ratio) by use of a micro film original and a commercially available photographic enlarger, and then developed using a + liquid developer. This was followed by the same treatment as that described in Example 9 to obtain a printing plate exhibiting a sharp image.

Example 12

The printing plate material obtained in Example 10 was treated to form a printing plate in the same way as described in Example 11, except that a He-Ne laser was used as the light source. In this way, a printing plate exhibiting a sharp image was obtained.

Example 13

The following coating composition was applied on the support used in Example 8 to a thickness of 3 μ after drying to obtain a printing plate material comprising the support having a polymeric layer thereon.

Epoxy Resin	10 parts by weight
Victoria Pure Blue 30H	0.1 parts by weight
Ethylcellosolve	90 parts by weight

A photosensitive material using zinc oxide on the market was negatively charged using corona discharge equipment, and exposed imagewise to a light source consisting of ten 20 W fluorescrnt lamps through a lens system by use of a reflection positive original. The electrostatic latent image thus formed was then toner-developed using a polystyrene-based toner and by the magnet brush process. The resulting toner image was then transferred onto the polymeric layer.

The toner-image on the polymeric layer was fixed with heat. The polymeric layer in non-image area was removed with methylcellosolve.

Printing plate thus obtained was used for printing with an offset press and this printing plate yielded 250,000 satisfactory prints having a sharp image.

Example 14

A colloid solution prepared as described below was uniformly applied as a physical development necleus onto the support made as described in Example 8, and dried to prepare a printing plate material.

Preparation of physical development nucleus:

Liquid A:	Palladium chloride	2 g
	Hydrochloric acid	35 ml
	Made up to 500 ml with water.	
Liquid B:	Na_2S	4 g
	10 % saponin	30 ml
	Made up to 500 ml with water.	
Liquid C:	15 % of copolymer of methyl vinyl ether and maleic anhydride	50 ml
	Gelatin	30 g
	Made up to 500 ml with water.	

Liquids A and B were mixed with violent stirring at room temperature, after addition of liquid C stirred for 5 minutes, and cooled to prepare a palladium sulfide physical development nucleus. Appropriate amounts of saponin as a surface active agent and formalin as hardening agent were then added, respectively, and the obtained mixture was applied onto the support to a wet thickness of 30 μ.

On the other hand, a photosensitive material was prepared by applying a high contrast silver chloride bromide emulsion, which was prepared according to a usual procedure, onto a photographic polyester film, followed by drying. The thus prepared photosensitive material was then used to photograph a positive original by use of a process camera. The photosensitive element exposed in this way was then contacted to the physical development nucleus layer, and developed for 60 seconds by use of the developing solution having the following composition:

Developing solution:

Phenidone	1.0 g
Anhydrous sodium sulfite	50 g
Hydroquinone	12 g
Sodium hydroxide	15 g
Sodium thiosulfate	5 g

Made up to 1 liter with water.

When the photosensitive material was separated from the physical development nucleus layer a clear mirror surface-like positive image was obtained on the printing plate having the physical development nucleus layer. The thus obtained plate was then wiped with a 5 % methanolic solution of 1-p-ethoxyphenyl-5-mercaptotetrazole as an agent for imparting ink receptivity. When the thus treated plate was then used immediately for printing by use of a printing ink, 80,000 satisfactory prints were obtained.

Example 15

A negative printing plate material was made by the diffusion-transfer process as described below by using the support obtained in the same way as in Example 9.

(a) Preparation of photosensitive silver halide emulsion:

A silver iodide bromide emulsion (silver iodide: 5 mol %) was prepared from silver nitrate, potassium bromide and potassium iodide. The emulsion was then chemically sensitized by the gold-sulfur sensitizer. Then, 0.3 g of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene per mol of silver halide was added as a stabilizer to the chemically sensitized emulsion to prepare a silver iodide bromide emulsion having a moderate sensitivity.

(b) Preparation of easily-soluble metal salt particles:

A pure silver chloride emulsion was prepared from silver nitrate and sodium chloride, and cleaned by sedimentation. Then, 0.6 g of 1-phenyl-5-mercapto-tetrazole per mol of silver chloride was added to the emulsion to make it sparingly soluble.

The previously prepared photosensitive silver halide emulsion (a) was mixed with the thus prepared sparingly-soluble pure silver chloride emulsion (b). After adding an appropriate amount of saponin as a surface active agent to the obtained mixture, the mixture was applied onto the aforesaid physical development nucleus layer used in Example 14 to prepare a printing plate material.

Both emulsions (a) and (b) were mixed together in a proportion of 0.2 mol of silver iodide bromide emulsion per mol of silver chloride emulsion on the silver basis.

A negative original film was brought into close contact with the silver halide emulsion layer, exposed and developed with a developing solution having the composition described below at a temperature of 30 °C for 90 seconds. Then, the printing plate material was dipped in running water at a temperature of 20 °C for 30 seconds to remove the upper silver halide layer.

[Composition of developing solution]:

Hydroquinone	12.0 g
Anhydrous sodium sulfite	50.0 g
Phenidone	1.2 g
Potassium hydroxide	11.0 g
Sodium thiosulfate	3.5 g
Anhydrous sodium sulfate	50.0 g
Potassium bromide	1.0 g
1-Phenyl-5-mercaptotetrazole	0.01 g

Made up to 1 liter with water.

The obtained printing plate was treated to impart ink receptivity as described in Example 14, and then immediately used for printing with an ink. The results were as shown below.

Prints before stains disappear	Printing life
5	More than 40,000 prints

(The printing press used was TOKO Model 810. The values in the "prints before stains disappear" column were determined by supplying an excess of the ink so that the whole surface of the printing plate was inked, stopping to supply the ink, and printing until the stains disappeared).

The results set forth in the above table clearly show that the printing plate using the support of this invention exhibits excellent water holding property and high printing life.

Example 16

The photopolymerizable composition having the composition described below was whirl-coated onto the support obtained in accordance with Example 2, and dried at a temperature of 50 °C for 10 minutes. The silicone layer had a thickness of 6 μ in dry state.

Co-condensation product of acryloxypropyltrichlorosilane and α,ω-dihydroxydimethyl organopolysiloxane (compound exemplified in Japanese Unexamined Patent Publication No. 47997/1973)	100 parts by weight
4-Dimethylamino-4'-trimethylsilylbenzophenone	5 parts by weight
Toluene	1000 parts by weight

Thereafter, a positive transparent original was brought into close contact with the thus coated support in a vacuum, and exposed to 2 kW Idle Fin at a distance of 1 m for 90 seconds. It was then developed with a developing solution comprising 100 parts of toluene and 150 parts of cyclohexane. Thus a printing plate in which the unexposed area was dissolved and removed was obtained.

The thus obtained printing plate was set on an offset press (Komori Sprint L-25B) and used for printing by using the coated paper, a dry offset color printing ink (BOWERS available from Printing Ink Company) and by removing the damping water feeder. Thus 200,000 high-quality prints were obtained.

Comparative Example 3

A printing plate material was made in the same way as described in Example 16, except that an electrochemically grained and anodized aluminium plate was used instead of the support in Example 1. When this printing plate was used for printing in the same manner as Example 16, the silicone rubber at the non-image area peeled off from the substrate and caused the surface of the support to be scumed after 50,000 prints were produced.

Example 17

The photosensitive solution having the composition described below was wire bar coated onto the support obtained in accordance with the procedure described in Example 9 , and dried at a temperature of 100 °C for 3 minutes.

Co-condensation product of bisphenol A, propylene oxide and maleic anhydride (Polylight TDR-1131R available from Dainippon Ink And Chemicals, Incorporated in Japan)	40 parts by weight
Addition product of 4 moles of glycidyl methacrylate and 1 mole of xylylene diamine	55 parts by weight
Benzoin methyl ether	5 parts by weight
Cellosolve acetate	700 parts by weight

The thickness of the obtained layer was 8 µ. Then, the silicone rubber solution set forth below was wire bar coated onto the thus obtained photosensitive layer, and dried at a temperature of 50 °C for 3 minutes.

Silicone Rubber YE-3085 (50 % solution, avilable from Toshiba Silicone K. K. in Japan)	12 parts by weight
Benzoin isopropyl ether	0.3 parts by weight
n-Heptane	88 parts by weight

The thickness of the obtained silicone rubber layer was 2 μ. The surface of the thus formed silicone rubber layer was laminated with a 6 μ-thick polyethylene terephthalate film (Lumilar available from Toray Industries Inc. in Japan) to obtain a photosensitive lithographic printing plate material.

Thereafter, a positive film was brought into close contact with the obtained printing plate material in a vacuum, and exposed to a 2 kW Idle Fin lamp at a distance of 1 m for 60 seconds. The Lumilar film was then peeled off, and the plate was developed in a n-heptane solution to give a lithographic printing plate. When used for printing under the same printing conditions as in Example 16, this printing plate yielded 250,000 high-quality prints.

Example 18

A support was made according to the procedure in Example 2. The obtained support was set at the printing section of the automatic proof machine KF-122-E available from Dainippon Screen Mfg. Co., Ltd. An original plate, which was made by exposing through a 150-line dot image original on the Sakura PS off-set plate SMP (available from Konishiroku Photo Industry Co., Ltd.), developed and processed, was used. In this way, the image was transferred to the support by printing. The transfer ink was an ultraviolet-curing ink (Dye Cure available from Dainippon Ink And Chemicals, Incorporated). After the transfer, the support was subjected to the exposure curing treatment by use of a 2 kW high-pressure mercury vapor lamp at a distance of 60 cm to obtain a duplicate printing plate.

When used for producing 50,000 prints with a roll-fed offset printing press, the thus obtained duplicate printing plate yielded satisfactory prints which exhibited a good image and sharply reproduced the 2 % dot of the original plate. Even when the amount of wetting water was reduced during printing, defects such as scumming and ink spreading at dots portion did not occur. Further, the quality of the print at the end of printing was almost the same as that obtained at the beginning of printing.

The printing plate used in the printing as described above was then allowed to stand for 3 months and again used for printing. In this case, the printing plate showed no rust and yielded prints of almost the same quality as that obtained before it was allowed to stand. Examination after printing of the gripped section of the printing plate revealed that the section did not damaged due to gripping and there was no risk of gripping failure.

Comparative Example 4

A duplicate printing plate was made in the same way as described in Example 18, except that a conventional chromium-plated iron plate (Tin Free available from Nippon Steel Corporation) was used instead of the support of this invention.

Since this chromium-plated iron plate was not sufficiently clean, it was degreased in advance in an aqueous 5 % sodium metasilicate solution at a temperature of 40 °C for 4 minutes, followed by washing with water and drying. The iron plate was then dipped in an aqueous potassium permanganate solution at room temperature for 1 minute and then in an aqueous 1 % oxalic acid solution at room temperature for 1 minute, followed by washing with water and drying. In this way, the iron plate was cleaned, activated and then used for making the duplicate printing plate.

Up to the step for making the duplicate printing plate, no significant difference was observed compared with Example 14. However, in the printing by use of this printing plate, the non-image area was scummed immediately after the printing was started, because of insufficient hydrophilicity and water receptive ability of the printing plate. In addition, after about 1,500 prints were produced, the image area was damaged and ink receptivity deteriorated so that normal prints could not be obtained any more.

Comparative Example 6

A duplicate printing plate was made in the same way as described in Example 14, except that a brush-grained aluminium plate described below was used instead of the support.

The brush-grained aluminium plate was made as follows: A 0.24 mm-thick 3S aluminium plate was grained by use of a nylon brush and an aqueous suspension of 400 mesh pumice powder, and thoroughly washed with water. Then, the aluminium plate was subjected to etching in an aqueous 10 % sodium hydroxide solution at a temperature of 50 °C for 20 seconds. The aluminium plate was then desmutted in a 30 % nitric acid solution at room temperature for 20 seconds. Thereafter, the aluminium plate was anodized in a sulfuric acid solution at a temperature of 40 °C for 15 minutes at a voltage of 20 V and a current density of 3 A/dm^2. The roughness of the obtained grains was Rz 5.5 μ, Ra 0.9 μ (DIN standard). The amount of the anodized film was 40 mg/dm^2.

Claims:

1. A support for lithographic printing plate, comprising an electrodeposited chromium layer having protuberant portions on an iron material with a center line average roughness (Ra) of 0.1 to 3 µm.

2. The support for lithographic printing plate according to Claim 1, wherein the protuberant portions have a projected area percentage of 20% or more.

3. The support for lithographic printing plate according to Claim 1, wherein the electrodeposited chromium layer has crystalline products with angles and/or an agglomerated product thereof.

4. The support for lithographic printing plate according to Claim 3, wherein the crystalline products are in the shape of plates or hexahedrons.

5. The support for lithographic printing plate according to Claim 4, wherein the crystalline products are in the shape of hexagonal plates or cubes.

6. The support for lithographic printing plate according to Claim 5, wherein the plates are 0.5 to 5 µm in diameter and 0.01 to 0.8 µm in thickness.

7. The support for lithographic printing plate according to Claim 5, wherein the cubes are 0.1 to 2 µm in side length.

8. The support for lithographic printing plate according to Claim 1, wherein Ra is 0.3 to 2 µm.

FIG.1

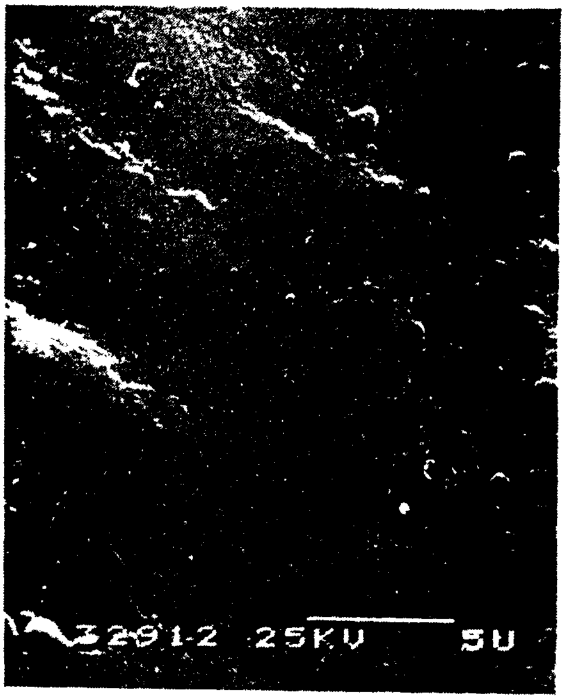


FIG.2

F I G.3

F I G.4