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EUROPEAN PATENT SPECIFICATION

⑬ Date of publication of patent specification: **21.09.88**

⑭ Int. Cl.⁴: **C 22 C 21/00, B 41 N 1/08**

⑮ Application number: **83105393.9**

⑯ Date of filing: **31.05.83**

⑰ **Aluminium alloy, a support of lithographic printing plate and a lithographic printing plate using the same.**

⑱ Priority: **01.06.82 JP 92079/82**
01.06.82 JP 92080/82

⑲ Date of publication of application:
21.12.83 Bulletin 83/51

⑳ Publication of the grant of the patent:
21.09.88 Bulletin 88/38

㉑ Designated Contracting States:
DE FR GB

㉒ References cited:
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CHEMICAL ABSTRACTS, vol. 98, 1983, page
281, no. 184150b, Columbus, Ohio, US

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Description

The present invention relates to a lithographic printing plate support, a lithographic printing plate using the same and methods for their production.

5 When using aluminum plates as supports for printing plates, they are usually subjected to a treatment for roughening their surfaces in order to ensure good intimate adhesion between the aluminum plate and a light-sensitive film to be provided thereon and improve water retention in non-image areas. This surface roughening treatment is called graining, and includes mechanical graining such as ball graining, sand blast graining or brush graining, electrochemical graining which is also called electrolytic polishing, and
10 chemical etching which is called chemical graining. These conventional graining processes possess advantages and disadvantages. In general, problems with the mechanical graining process include scuff marks, stains and residue of an abrasive used. The electrochemical graining process makes it possible to change the depth of the graining as well as the form of grains by controlling the quantity of electricity. However, it requires a large quantity of electricity and a long time to create grains suited for printing plates
15 which leads to high production costs.

On the other hand, the chemical graining process grains aluminum or aluminum alloy by a chemical etching reaction using an acid or an alkali etchant, and, hence, it is simple and suited for continuously treating aluminum or aluminum alloy strips, and is particularly advantageous for industrially producing plates having been treated on both sides.

20 However, it has so far been difficult to produce high quality printing plates using commercially available aluminum or aluminum alloy. Conventional chemical etching processes, for example, described in U.S. Patents 2,344,510 and 2,714,066, have difficulty in forming a surface having enough surface roughness and uniform pit pattern (wherein etching pits have a uniform diameter and a uniform depth) to give sufficient printing durability and staining resistance required for printing plates.

25 According to the experiments conducted by the inventors, chemical etching of commercially available aluminum and aluminum alloy (JIS 1050, 1100 and 3003) using various etchants has been found to involve the following problems. (1) It is difficult to provide a practical surface roughness of 0.3 to 1.2 μ Ra (center line average roughness) which is suitable as a printing plate and, even when such roughness is attained, the reaction rate is so slow that the process requires a long time. (2) The etchant contains ingredients
30 harmful for workers, thus causing a problem in view of working atmosphere. (3) The etching cost is too high to be practical.

GB—A—2047274 discloses a support for a lithographic printing plate prepared by mechanically graining the surface of an aluminum alloy plate, chemically etching the plate with an etching solution (acid or alkali) and electro-mechanically etching in an acidic electrolytic solution. The plate can further be
35 provided with an anodic oxidation film and/or with a light sensitive layer. Aluminum alloys contain Fe, Zn, Cu, Mg, Si, Mn, Cr and Ti as alloying elements.

It is the object of the present invention to provide a lithographic printing plate support which is capable of forming uniformly and densely distributed pits thereon by an etching treatment with a small quantity of aluminum dissolution and obtaining a desired surface roughness, and a lithographic printing plate using
40 the same as well as methods for producing same.

Said object is achieved by a support for a lithographic printing plate, comprising an aluminum alloy material containing Fe and optionally Cu and/or Mg and further alloying components besides Al, characterized in that it consists of 0.20 to 1.0% Fe, 0.005 to 0.1% of at least one element selected from the group consisting of Sn, In and Ga, optionally 0.1 to 2% Cu and/or 0.1 to 0.6% Mg and balance Al and a light-
45 sensitive lithographic printing plate comprising said support, having provided thereon a light-sensitive layer.

Said object is further achieved by a method for producing said support characterized by the steps of a) providing an aluminum alloy material as defined in Claim 1, b) subjecting a surface of the aluminum alloy material to a chemical etching treatment with a solution of an acid or an alkali; and c) subjecting the surface
50 to an electrochemical etching treatment in an acidic electrolytic solution and a method for producing a light-sensitive lithographic printing plate characterized in that it comprises a) providing an aluminum alloy material as defined in Claim 1, b) subjecting a surface of the aluminum alloy material to a chemical etching treatment, with a solution of an acid or an alkali; c) subjecting the surface to an electrochemical etching treatment in an acidic electrolytic solution; and d) providing a light-sensitive layer on the uniform and
55 dense grain structure in the surface.

The aluminum alloy used in the present invention shows a good solution velocity for chemical etching treatment and contains an intermetallic compound capable of accelerating formation of uniform pits. Etching treatment of the plate with a popularly used acid or alkali produces uniformly and densely distributed pits on the surface of the plate.

60 The alloy composition used in the present invention is described below.

In order to accelerate solution velocity of aluminum, it is desired to first enlarge the local cathode area as large as possible, then to render the local anode less precious. For the first purpose, incorporation of much impurities is recommended. Addition of 0.20 to 1.0% of Fe and, preferably, further addition of 0.1 to 2% of Cu and/or 0.1 to 0.6% of Mg has been found to be effective. (In the present specification, percents are
65 expressed by weight unless otherwise stated.) If the content of Fe and Cu and/or Mg is higher than

described above, the anode area is reduced, resulting in formation of a non-uniform etching pit pattern. In addition, an anode oxidation film is difficult to produce on impurities, and, hence, incorporation of too much impurities would cause film defects, resulting in the formation of background stain upon printing. Alloys containing Fe and, optionally, Cu and/or Mg show such a large solution velocity for both acids and alkalis that a proper solution can be selected depending upon the amount of etching desired and the desired pattern.

Addition of such elements as Sn, In and Ga renders a matrix electrochemically less precious, thus accelerating solution velocity. Plates containing these elements may be employed for relief printing plates disclosed in Japanese Patent Publication No. 9930/74. With relief printing plates, a pattern with a depth of several mm is required, whereas with lithographic plates the depth is several μm at most, which means that the pit pattern must be fine.

It has been surprisingly found that addition of small amounts of Sn, In and Ga as described above to Fe and, optionally Cu and/or Mg, alloys renders the resulting pit pattern extremely fine though solution velocity is not substantially influenced. These elements are added in an amount in the range of 0.005 to 0.1%.

If the elements Sn, In and Ga are added in amounts greater than 0.1%, the solution limit is exceeded to the extent that local dissolution becomes a problem making it difficult to form a uniform pit pattern.

The aluminum alloy used in the present invention is produced by hot-rolling of a casting composition for aluminum alloy containing Al, Fe and at least one element selected from among Sn, In and Ga and optionally Cu and/or Mg, at 400°C to 600°C, and intermedium-annealing at 300°C to 500°C followed by cold-rolling to obtain a desired thickness. Aluminum and other contents in the alloy thus-obtained were identified using fluorescence X-ray analysis and/or emission spectroanalysis.

The printing plate support in accordance with the present invention is produced as follows.

The support comprising the alloy is subjected to at least one chemical etching step optionally followed by an electrochemical etching step.

The chemical etching of the aluminum alloy is carried out using an acid such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid or hydrofluoric acid, or a mixture of two or more of these acids, and an alkali such as sodium hydroxide, sodium carbonate, sodium tertiary phosphate or sodium silicate.

Concentration and temperature of the etching solution depend upon the etching time and required surface roughness but, as a general guide, the concentration ranges from 1 to 50%, the temperature from 20°C to 90°C and the treating time from 10 s to about 4 min. Both chemical etching by alkali and acid may be carried out in this order or in the reverse order. Where the plate is stained, for example; with a rolling oil, a degreasing treatment is conducted prior to the chemical etching. In order to remove smut remaining on the etched surface, pickling is effected. Acids to be used for the pickling include nitric acid and sulfuric acid. The pickling reaction can be accelerated by adding hydrogen peroxide.

The surface of the thus-treated aluminum plate must have uniformly and densely distributed pits having an average depth of 1 to 10 μm which corresponds to an average roughness of 0.3 to 1.2 μm (presented as Ra) and an opening diameter of 1 to 10 μm .

The average depth of pits is an important parameter in determining surface roughness and a uniform pit pattern is necessary for attaining printing durability and staining resistance required for printing plates. If the pit depth is less than 1 μm , the surface roughness is limited to 0.2 μm (Ra) at the highest which fails to give high printing durability and enough water retention to the resulting printing plate. On the other hand, if the pit depth is more than 10 μm , the surface roughness exceeds 1.2 μm (Ra) and staining resistance tends to be deteriorated. In addition, it becomes substantially difficult to form an uniform etching pit pattern wherein the pits have an uniform diameter and an uniform depth, and the amount of etched aluminum is increased, resulting in an unpractically high etching cost.

The base plate having an average roughness of 0.3 to 1.2 μm (Ra) can itself be practically used as a lithographic printing plate by providing thereon an anodically oxidized film to strengthen corrosion resistance and abrasion resistance of the surface. however, under severe printing conditions or for conducting printing with high quality such as color printing, the plate is further improved in view of printing durability, staining resistance, and tone reproducibility.

As a result of intensive investigations, the inventors have found that a support for a lithographic printing plate having improved printing durability, staining resistance, and tone reproducibility can be produced by subjecting the above-described surface to an electrochemical etching treatment in an electrolytic solution containing hydrochloric acid or its salt, nitric acid or its salt, or a mixture thereof using DC or AC. Concentration of the acid or salt thereof in the electrolytic solution is preferably 0.1 to 100 g, more preferably 0.5 to 60 g, per liter of the electrolytic solution. The temperature of the electrolytic solution ranges preferably from 20°C to 60°C, and the treating time from 1 s to 10 min preferably 3 s to 5 min. Conditions of electrochemical etching depend on required surface roughness and pit pattern of the support. Observation of the surface of the thus-obtained support under a scanning type electron microscope (SEM) revealed that secondary pits having an average opening diameter of 5 μm or less were uniformly and superimposedly distributed. In addition, a section of the support was prepared by using a microtome, and the profile of the section was surveyed under the scanning electron microscope to find that the average depth of the pits was 1 μm or less. Samples having widely varying diameters and depths of pits can be prepared by properly selecting the kind of electrolytic bath, kind of source of electric power, and

electrolysis conditions. The support thus-obtained by the electrochemical etching treatment has an average roughness of 0.3 to 1.2 μm (Ra) which is almost the same value as the support obtained by the chemical etching.

As a result of detailed investigations, the inventors have found that the best balanced performance including printing durability, staining resistance, tone reproducibility, etc., can be obtained by forming the secondary pits having an opening diameter of 5 μm or less or a depth of 1 μm or less on the surface having the primary pits of 1 to 10 μm in depth. If the pits have an opening diameter of more than 5 μm or a depth of more than 1 μm , the primary pits are destroyed and suffer reduction of substantial pit depth, adversely affecting printing durability and water retention.

Formation of the secondary pits by electrochemical etching can be effected by using an electrolytic bath of either hydrochloric acid or nitric acid. In order to render the pit diameter uniform, electric current of a special alternating wave described in U.S. Patent 4,087,341, compounds such as amines described in U.S. Patent 3,755,116, sulfuric acid described in Japanese Patent Application (OPI) No. 57902/74 (the term "OPI" as used herein refers to a "published unexamined Japanese patent application"), boric acid described in U.S. Patent 3,980,539, phosphoric acid shown in West German Patent Application (OLS) 2,250,275 and U.S. Patent 3,887,447, may be employed or added.

Stains remaining on the electrochemically etched surface can be removed by contacting the surface with 50 to 90°C, 15 to 65 wt% sulfuric acid as described in Japanese Patent Application (OPI) No. 12739/78 or by etching with an alkali described in Japanese Patent Publication No. 28123/73.

The thus-treated aluminum alloy plate can be used as such as a support for a lithographic printing plate. In addition, an anode oxidation film may further be provided thereon to use as a high quality lithographic printing plate support. The thickness of the anode oxidation film is preferably 0.1 to 10 g/m^2 , more preferably 0.1 to 5 g/m^2 .

The anodic oxidation processing can be carried out using techniques which have so far been employed in the art. Specifically, an anodically oxidized film can be formed on the surfaces of an aluminum support by passing DC or AC current to the aluminum support in an aqueous solution containing sulfuric acid, phosphoric acid, oxalic acid, or a mixture of two or more of these acids. Anodizing conditions are changed depending upon what kind of electrolytic solution is used and, therefore, they cannot be determined indiscriminately. However, as a general guide, it can be said that an electrolytic solution having a concentration of 1 to 80 wt%, a solution temperature of 5 to 70°C, a current density of 0.5 to 60 A/ dm^2 , a voltage applied of 1 to 100 V and an electrolyzing time of 10 to 100 s can produce a preferable result.

Particularly effective anodically oxidized film forming processes are the processes used in British Patent 1,412,768, wherein anodic oxidation is carried out in sulfuric acid by sending a high density electric current and the process described in U.S. Patent 3,511,661 (incorporated herein by reference to disclose a process), wherein anodic oxidation is carried out using phosphoric acid as an electrolytic bath. The thickness of the anodically oxidized film is preferably 0.1 to 10 g/m^2 , more preferably 0.1 to 5 g/m^2 .

The aluminum plate which has been anodically oxidized may be further treated with an aqueous solution of an alkali metal silicate such as sodium silicate or the like using a conventional technique, e.g., a dipping technique, as described in U.S. Patents 2,714,066 and 3,181,461 (incorporated herein by reference to disclose such techniques). Alternatively, a subbing layer made up of hydrophilic cellulose (e.g., carboxymethyl cellulose,) containing a water-soluble metal salt (e.g., zinc acetate) and in a preferable thickness of 0.001 to 1 g/m^2 , more preferable a thickness of 0.005 to 0.5 g/m^2 , may be additionally provided on the anodically oxidized aluminum plate, as described in U.S. Patent 3,860,426 (incorporated herein by reference to disclose how to provide a subbing layer).

A light-sensitive layer which is known for presensitized plates is provided on the lithographic printing plate support prepared in accordance with the present invention to produce a light-sensitive lithographic printing plate. The lithographic printing plate obtained by subjecting this presensitized plate to a plate making process has excellent properties.

Suitable examples of the composition of the above-described light-sensitive layer are described below.

(1) Light-sensitive layer comprised of a diazo resin and a binder:

Preferred examples of the diazo resin include those described in U.S. Patents 2,063,631, 2,667,415, Japanese Patent Publication Nos. 18001/74, 45322/74, 45323/74 and British Patents 1,312,925 and 1,023,589. Preferred examples of the binder include those described in British Patents 1,350,521 and 1,460,978, U.S. Patents 4,123,276, 3,751,257, and 3,660,097, and Japanese Patent Application (OPI) No. 98614/79 (the term "OPI" as used herein refers to a "published unexamined Japanese Patent Application").

(2) Light-sensitive layer comprised of an o-quinonediazide compound:

Particularly preferable examples of the o-quinonediazide compound include o-naphthoquinonediazide compounds as described in U.S. Patents 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 many other publications.

(3) Light-sensitive layer comprised of a composition containing an azide compound and a binder (macromolecular compound):

Specific examples of the composition include compositions comprised of azide compounds and water soluble or alkali-soluble macromolecular compounds which are described in British Patents 1,235,281 and 1,495,861, Japanese Patent Application (OPI) Nos. 32331/76 and 36128/76, and compositions comprised of

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azido group-containing polymers and macromolecular compounds as binders, as described in Japanese Patent Application (OPI) Nos. 5102/75, 84302/75, 84303/75, and 12984/78.

(4) Light-sensitive layers comprised of other light-sensitive resinous compositions.

Specific examples include the polyester compounds disclosed in Japanese Patent Application (OPI) No. 96696/77, polyvinyl cinnamate series resins described in British Patents 1,112,277, 1,313,390, 1,341,004 and 1,377,747 and photopolymerizable photopolymer compositions described in U.S. Patents 4,072,528 and 4,072,527.

The amount (thickness) of the light-sensitive layer to be provided on the support is controlled to about 0.1 to about 7 g/m², preferably 0.5 to 4 g/m².

Lithographic printing plates, after imagewise exposure, are subjected to proceedings including a developing step in a conventional manner to form resin images. For instance, a lithographic printing plate having the light-sensitive layer (1) constituted with a diazo resin and a binder has unexposed portions of the light-sensitive layer removed by development after imagewise exposure to produce a lithographic printing plate. On the other hand, a lithographic printing plate having a light-sensitive layer (2) has exposed portions of the light-sensitive layer which are removed by development with an alkaline aqueous solution after imagewise exposure to produce a lithographic printing plate.

The present invention will now be described in more detail by reference to the following examples.

Unless otherwise stated, all percents (%) are by weight in the above description and in the following examples.

Example 1

A casting composition containing 99.26% of Al, 0.70% of Fe and 0.04% of Sn was subjected to hot-rolling, which temperature was 500°C, and then to intermedium-annealing at 400°C followed by cold-rolling. The aluminum alloy plate thus-obtained had 0.30 mm of thickness. The alloy was confirmed to contain 99.26% of Al, 0.70% of Fe and 0.04% of Sn by a fluorescence X-ray analysis using X-ray.

In the same way, the alloys of the present invention and the comparative alloys were obtained as is shown in the following Table 1.

Table 1

Alloy Composition (weight %)								
Alloy No.	Al	Fe	Cu	Mg	Sn	In	Ga	
Comparison 1'	99.20	0.80	-	-	-	-	-	
2'	98.80	0.70	0.50	-	-	-	-	
3'	99.85	0.10	-	-	0.05	-	-	
Present Invention 1	99.46	0.70	0.50	-	0.04	-	-	
2	98.74	0.70	0.50	-	-	0.06	-	
3	98.97	0.70	0.30	-	-	-	0.03	
4	99.75	0.20	-	-	0.05	-	-	
5	99.06	0.30	0.60	-	0.04	-	-	
6	99.26	0.70	-	-	0.04	-	-	
7	99.10	0.85	-	-	0.05	-	-	
8	98.91	0.83	-	0.21	0.05	-	-	

Example 2

The following aluminum alloy plates were prepared and subjected to a chemical graining treatment for 1 min at 60°C in 10% NaOH. Surface roughness of the thus-treated plates was measured, and the pit pattern was observed under a scanning electron microscope (SEM).

Samples were numbered to combine an alloy number with an etching process employed, for example, alloy No. 1 treated by etching process of Example 2 was called Sample No. 1A.

Table 2

No.	Aluminum Dissolution Amount g/m ²	Surface Roughness μm	Surface Appearance Opening Diameter
Comparison			
1'A	26	0.37	non-uniform pit pattern, coarse pits of 7 to 15 μm
2'A	27	0.34	Same as above
3'A	21	0.19	uniform pit pattern, slightly coarse pits of 2 to 8 μm
Present Invention			
1 A	27	0.35	uniform pit pattern 2 to 8 μm pits
2 A	27	0.33	Same as above
3 A	26	0.30	"
4 A	23	0.30	"
5 A	24	0.37	"
6 A	27	0.34	"
7 A	28	0.34	"
8 A	21	0.51	"

As is apparent from the Table 2, Sample No. 8A containing Fe and Mg as a main component has pit patterns having 2 to 8 μm of opening diameter and 0.45 μm or more of average surface roughness.

On the other hand, Sample Nos. 1A to 7A which contain Cu but do not contain Mg have uniform pit patterns having 2 to 8 μm of pit diameter. Those samples have a considerably good surface-appearance in comparison with Comparative Samples. Values of average surface roughness are slightly low in comparison with Samples containing Mg.

Then, Sample Nos. 1'A, 2'A and 3'A and Sample Nos. 1 to 3A and 5A and 8A were subjected to an electrochemical etching treatment in a 7 g/l nitric acid aqueous solution in an electricity amount of 100 Cb/dm² using a special alternating wave current described in Japanese Patent Application (OPI) No. 67507/78, then subjected to desmutting treatment of dipping in a 30% H₂SO₄ aqueous solution at 55°C for 1 min. Subsequently, a 3g/m² thick oxide film was formed thereon in an electrolytic solution containing 20% sulfuric acid as a major component at a temperature of 30°C, followed by dipping in a 2.5% aqueous solution of JIS No. 3 sodium silicate at 60°C for 1 min, thoroughly washing with water, and drying.

Surface roughness of each of the thus-obtained samples was determined, and their pit patterns were

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observed under a scanning electron microscope (SEM) to determine the opening diameter. Also, a section of each sample prepared by a microtome was observed under SEM to measure the pit depth.

Results thus-obtained are tabulated in Table 3.

Table 3

No.	Surface Roughness	Depth of Secondary Pits (μm)	Opening Diameter of Secondary Pits (μm)
Present Invention	1B	0.35	0.1 ~ 0.8
	2B	0.34	"
	3B	0.32	"
	5B	0.38	"
	6B	0.37	"
	7B	0.37	"
	8B	0.51	"
Comparison	1'B	0.38	"
	2'B	0.36	"
	3'B	0.20	"

Sample Nos. 1B to 8B and Sample Nos. 1'B to 3'B had secondary pits of 0.1 to 0.8 μm of depth and 1 to 3 μm of opening diameter.

The surface roughness was the same as that of samples treated by alkali etching process shown in Table 1.

Example 3

On the supports base comprising Sample Nos. 6A and 6B, and Comparative Sample No. 3'B obtained in Example 1 was coated the following light-sensitive layer in a dry thickness of 2.0g/m².

2-Hydroxyethyl methacrylate copolymer (synthesized according to the process described in Example 1 of British Patent 1,505,739)	0.7 g
2-Methoxy-4-hydroxy-5-benzoylbenzene- sulfonate of a condensate between p- diazophenylamine and paraformaldehyde	0.1 g
Oil Blue #603 (product of Orient Chemical Co., Ltd.)	0.03 g

2-Methoxyethanol	6 g
Methanol	6 g
Ethylenedichloride	6 g

The thus-obtained light-sensitive lithographic printing plates were each imagewise exposed for 70 s by means of a metal halide lamp of 3 KW placed at a distance of 1 m and dipped in the following developing solution for 1 min at room temperature. Then, the surface of each plate was lightly rubbed by an absorbent wadding to remove unexposed areas, thus lithographic printing plates were obtained, respectively.

Formulation of Developing Solution:

Sodium sulfite	3 g
Benzyl alcohol	30 g
Triethanolamine	20 g
Monoethanolamine	5 g
Pelex NBL (sodium t-butyl-naphthalene-sulfonate; product of Kao Atlas Co., Ltd.)	30 g
Water	1,000 ml

Then, printing was conducted in a conventional manner to obtain results shown in Table 4.

Table 4

Plate	6A	6B	3'B
Support	6A	6B	3'B
Primary pits:			
Average Depth (μm)	1 ~ 10	1 ~ 10	1 ~ 6
Opening Diameter (μm)	2 ~ 8	2 ~ 8	2 ~ 8
Secondary pits:			
Average Depth (μm)	—	0.1 ~ 0.8	0.1 ~ 0.8
Opening Diameter (μm)	—	1 ~ 3	1 ~ 3
Amount of Electrochemically Etching Electricity (C/dm^2)	—	100	100
Weight of Anode Oxidation Film (g/m^2)	3.0	3.0	3.0
Surface Roughness (μm)	0.34	0.37	0.19
Printing Durability	80,000	130,000	100,000
Staining Resistance	excellent	excellent	fair

As is apparent from Table 4, a plate of No. 6B, having a support of No. 6B which was subjected to electrochemical etching treatment was extraordinarily improved in printing durability in comparison with a plate of No. 6A having a support of No. 6A which was not treated. Further, the plate of No. 6B was superior to the plate No. 3'B wherein the support is subjected to electrochemical etching.

It seems that the support of No. 3'B has a lower value in surface roughness.

Example 4

Sample No. 1 and comparative sample Nos. 2' and 3', shown in Example 1, were subjected to a first chemical graining treatment in 10% sodium hydroxide at 60°C for 1 to 5 min then to a second chemical graining treatment in an aqueous mixture solution of 300 ml/l nitric acid and 150 ml/l sulfuric acid at 90°C for 3 minutes, followed by observation under SEM and measurement of surface roughness.

Table 5

Properties of samples subjected to
two-stage graining treatments

<u>Sample</u>	<u>Time for First Treatment</u>	<u>Surface Roughness (μRa)</u>	<u>Pit Pattern</u>
1C ₁	1 min	0.40	uniform, mixed pattern of 2 - 8 μ m pits and 0.1 - 0.3 μ m pits
1C ₂	2 min	0.45	"
1C ₃	3 min	0.51	"
1C ₄	4 min	0.53	"
1C ₅	5 min	0.59	"
Compara- tive Ex.			
2'C ₅	5 min	0.57	non-uniform, 10 - 19 μ m coarse pits
3'C ₅	5 min	0.73	uniform

A plane with a large surface roughness was formed on sample Nos. 1C₁ to 1C₅ due to its large solution quantity for both acid and alkali. In addition, sample Nos. 1C₁ to 1C₅ had a multi pit pattern wherein uniform 1 to 5 μ m pits were formed with acid in uniform 2 μ m to 8 μ m pits having been formed with alkali.

Example 5

Sample No. 1A described in Example 2, comparative sample Nos. 2'A and 3'A and sample No. 1C₅ having been subjected to two-stage graining treatments in Example 4 were anodized in an electrolytic solution containing 20% sulfuric acid as a major component at a bath temperature of 30°C to provide thereon a 3g/m² oxide film, then dipped in a 2.5% aqueous solution of sodium silicate (JIS No. 3) at 60°C for 1 min, washed thoroughly with water, and dried.

The thus-treated samples prepared from sample No. 1A, comparative samples Nos. 2'A and 3'A, and sample No. 1C₅ were referred to as sample Nos. (1A), (2'A), (3'A) and (1C₅)D, respectively. On each of the thus-prepared samples was coated the solution used in Example 3 in a dry thickness of 2.0g/m² to prepare lithographic printing plates.

The thus-obtained light-sensitive lithographic printing plates were each imagewise exposed for 70 s by means of a metal halide lamp of 3 kW placed at a distance of 1 m, and dipped in the following developing solution for one minute at room temperature. Then, the surface of each plate was lightly rubbed by an absorbent wadding, to remove unexposed areas, thus printing plate Nos. (1A), (2'A), (3'A) and (1C₅)D were obtained, respectively.

Printing was then conducted in a conventional manner to obtain the results tabulated in Table 6.

Table 6

5	Sample	(1A)	(2'A)	(3'A)	(1C ₅)D
	Support	(1A)	(2'A)	(3'A)	(1C ₅)D
10	Surface Roughness (Ra)	0.35 μm	0.34	0.19 μm	0.51 μm
15	Degree of Uniformity of Pits	uniform, 2-8 μm pits	coarse, 7-15 μm pits (non-uniform)	uniform, 2-8 μm pits	mixture pattern of uniform 2-8 μm pits and 1-5 μm pits
	Printing Durability	80,000	50,000	20,000	100,000
20	Staining Resistance	excellent	fair	excellent	excellent

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Example 6

Sample No. 7A, and Comparative sample No. 1'A, shown in Example 2, were anodized in an electrolytic solution containing 20% sulfuric acid as a major component at a bath temperature of 30°C to provide thereon a 3g/m² oxide film, then dipped in a 2.5% aqueous solution of sodium silicate (JIS No. 3) at 60°C for 1 minute, washed thoroughly with water and dried.

30 The sample No. 7A. A thus treated and Comparative sample No. 1 were referred to as Support Nos. (7A)E, and (1'A)E, respectively.

On each of the supports thus prepared was coated the solution used in Example 3 to prepare lithographic printing plates.

35 The lithographic printing plates thus obtained were each imagewise exposed for 70 s by means of a metal halide lamp of 3 KW placed at a distance of 1 m and dipped in the developing solution shown in Example 3 for 1 min at room temperature. Then, the surface of each plate was lightly rubbed by an absorbent wadding, to remove unexposed areas, thus printing plates Nos. (7A)E and (1'A)E were obtained, respectively.

40 Printing was conducted in a conventional manner to obtain the results tabulated in Table 7.

Table 7

45	Sample	(7A)E	(1'A)E
	Support	(7A)E	(1'A)E
50	Surface Roughness (Ra)	0.34 μm	0.37 μm
55	Degree of Uniformity of Pits	uniform 2 to 8 μm pits.	non-uniform 7 to 15 μm coarse pits
	Printing Durability	70,000	50,000
60	Staining Resistance	excellent	fair

65 Sample No. (7A)E is superior to Sample No. (1'A)E in printing durability and staining resistance.

Claims

1. A support for a lithographic printing plate, comprising an aluminum alloy material containing Fe and optionally Cu and/or Mg and further alloying components besides Al, characterized in that it consists of
 - 0,20 to 1,0% Fe
 - 0,005 to 0,1% of at least one element selected from the group consisting of Sn, In and Ga, optionally
 - 0,1 to 2% Cu and/or
 - 0,1 to 0,6% Mg and
 - balance Al.
2. The support as claimed in Claim 1, characterized in that its surface is chemically etched or electrochemically etched.
3. The support as claimed in Claim 1, characterized in that its surface is chemically etched and electrochemically etched.
4. The support as claimed in Claim 2 or 3, characterized in that its surface is chemically etched with an etching solution of an acid selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, and hydrofluoric acid or an alkali solution selected from the group consisting of sodium hydroxide, sodium carbonate, sodium tertiary phosphate and sodium silicate.
5. The support as claimed in Claims 1—4, characterized in that its surface has an anode oxidation film or a subbing layer provided thereon.
6. The support as claimed in Claims 1—4, characterized in that its surface has an anode oxidation film and a subbing layer provided thereon.
7. The support as claimed in Claim 5 or 6, characterized in that the subbing layer is comprised of a hydrophilic cellulose containing a water-soluble metal salt.
8. The support as claimed in Claims 1—7, characterized in that the surface of said aluminum alloy material forms a rough plane having primary pits of 0,3 to 1,2 μm (presented as Ra) in average roughness or 1 to 10 μm in average depth.
9. The support as claimed in Claims 1—7, characterized in that the surface of said aluminum alloy material forms a rough plane having secondary pits of 1 μm or less in average depth and 5 μm or less in average opening diameter.
10. A light-sensitive lithographic printing plate, characterized in that it comprises a support according to Claims 1—9, having provided thereon a light-sensitive layer.
11. The light-sensitive lithographic printing plate as claimed in Claim 10, characterized in that the light-sensitive layer is present in an amount within the range of 0,1 to 7g/m².
12. The light-sensitive lithographic printing plate as claimed in Claim 11, characterized in that the light-sensitive layer is present in an amount within the range of 0,5 to 4g/m².
13. A method for producing the support for a lithographic printing plate as claimed in Claims 1—9, characterized by the steps of:
 - a) providing an aluminum alloy material as defined in Claim 1;
 - b) subjecting a surface of the aluminum alloy material to a chemical etching treatment with a solution of an acid or an alkali; and
 - c) subjecting the surface to an electrochemical etching treatment in an acidic electrolytic solution.
14. A method for producing a light-sensitive lithographic printing plate as claimed in Claims 10—12, characterized in that it comprises
 - a) providing an aluminum alloy material as defined in Claim 1
 - b) subjecting a surface of the aluminum alloy material to a chemical etching treatment, with a solution of an acid or an alkali;
 - c) subjecting the surface to an electrochemical etching treatment in an acidic electrolytic solution; and
 - d) providing a light-sensitive layer on the uniform and dense grain structure in the surface.

Patentansprüche

1. Träger für eine lithographische Druckplatte, der ein Aluminiumlegierungsmaterial, enthaltend Fe und gegebenenfalls Cu und/oder Mg und weitere Legierungskomponenten neben Al, umfaßt, dadurch gekennzeichnet, das er aus
 - 0,20 bis 1,0% Fe
 - 0,005 bis 0,1% wenigstens eines Elements, gewählt aus der Gruppe, bestehend aus Sn, In und Ga, gegebenenfalls
 - 0,1 bis 2% Cu und/oder
 - 0,1 bis 0,6% Mg und
 - als Rest Al besteht.

2. Träger nach Anspruch 1, dadurch gekennzeichnet, daß seine Oberfläche chemisch geätzt oder elektrochemisch geätzt ist
3. Träger nach Anspruch 1, dadurch gekennzeichnet, daß seine Oberfläche chemisch geätzt und elektrochemisch geätzt ist.
- 5 4. Träger nach Anspruch 2 oder 3, dadurch gekennzeichnet, daß seine Oberfläche mit einer Ätzlösung aus einer Säure, gewählt aus der Gruppe, bestehend aus Salzsäure, Salpetersäure, Schwefelsäure, Phosphorsäure und Flußsäure, oder einer alkalischen Lösung, gewählt aus der Gruppe, bestehend aus Natriumhydroxid, Natriumcarbonat, Natriumtertiärphosphat und Natriumsilikat, chemisch geätzt ist.
- 10 5. Träger nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß seine Oberfläche einen Anodenoxidationsfilm oder eine Grundsicht darauf besitzt.
6. Träger nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß seine Oberfläche einen Anodenoxidationsfilm und eine Grundsicht darauf besitzt.
7. Träger nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß die Grundsicht eine hydrophile Cellulose, enthaltend ein wasserlösliches Metallsalz, umfaßt.
- 15 8. Träger nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Oberfläche des Aluminiumlegierungsmaterials eine raue Ebene mit primären Gruben bzw. Löchern einer durchschnittlichen Rauheit von 0,3 bis 1,2 µm (dargestellt als Ra) oder einer durchschnittlichen Tiefe von 1 bis 10 µm bildet.
9. Träger nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die Oberfläche des Aluminiumlegierungsmaterials eine raue Ebene mit sekundären Gruben bzw. Löchern einer durchschnittlichen Tiefe von 1 µm oder weniger und einem durchschnittlichen Öffnungsdurchmesser von 5 µm oder weniger bildet.
- 20 10. Lichtempfindliche lithographische Druckplatte, dadurch gekennzeichnet, daß sie einen Träger nach einem der Ansprüche 1 bis 9 mit einer darauf vorgesehenen lichtempfindlichen Schicht umfaßt.
- 25 11. Lichtempfindliche lithographische Druckplatte nach Anspruch 10, dadurch gekennzeichnet, daß die lichtempfindliche Schicht in einer Menge im Bereich von 0,1 bis 7 g/m² vorliegt.
12. Lichtempfindliche lithographische Druckplatte nach Anspruch 11, dadurch gekennzeichnet, daß die lichtempfindliche Schicht in einer Menge im Bereich von 0,5 bis 4 g/m² vorliegt.
13. Verfahren zur Herstellung des Trägers für eine lithographische Druckplatte nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß
- 30 a) ein Aluminiumlegierungsmaterial gemäß Anspruch 1 vorgesehen wird;
- b) eine Oberfläche des Aluminiumlegierungsmaterials einer chemischen Ätzbehandlung mit einer Lösung aus einer Säure oder einem Alkali ausgesetzt wird und
- c) die Oberfläche einer elektrochemischen Ätzbehandlung in einer sauren Elektrolytlösung ausgesetzt wird.
- 35 14. Verfahren zur Herstellung einer lichtempfindlichen lithographischen Druckplatte nach einem der Ansprüche 10 bis 12, dadurch gekennzeichnet, daß
- a) ein Aluminiumlegierungsmaterial gemäß Anspruch 1 vorgesehen wird,
- b) eine Oberfläche des Aluminiumlegierungsmaterials einer chemischen Ätzbehandlung mit einer Lösung aus einer Säure oder einem Alkali ausgesetzt wird,
- 40 c) die Oberfläche einer elektrochemischen Ätzbehandlung in einer sauren Elektrolytlösung ausgesetzt wird und
- d) eine lichtempfindliche Schicht auf der gleichmäßigen und dichten Kornstruktur in der Oberfläche vorgesehen wird.
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Revendications

1. Support pour plaque d'impression lithographique, comprenant un matériau en alliage d'aluminium contenant Fe et le cas échéant Cu et/ou Mg et encore des composants pour alliage outre Al, caractérisé en ce qu'il est constitué par:
- 50 0,20 à 1,0% Fe
0,005 à 0,1% d'au moins un élément choisi dans le groupe constitué par Sn, In et Ga le cas échéant
55 0,1 à 2% Cu et/ou
0,1 à 0,6% Mg, et
le reste en Al.
2. Le support selon la revendication 1, caractérisé en ce que sa surface est décapée chimiquement ou électrochimiquement.
- 60 3. Le support selon la revendication 1, caractérisé en ce que sa surface est décapée chimiquement et électrochimiquement.
4. Le support selon la revendication 2 ou 3, caractérisé en ce que sa surface est décapée chimiquement par une solution de décapage d'un acide choisi dans le groupe constitué par l'acide chlorhydrique, l'acide nitrique, l'acide sulfurique, l'acide phosphorique, et l'acide fluorhydrique ou une solution d'un alcali choisi
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dans le groupe constitué par l'hydroxyde de sodium, le carbonate de sodium, le phosphate tertiaire de sodium et le silicate de sodium.

5. Le support selon les revendications 1—4, caractérisé en ce que sa surface porte un film, d'oxydation anodique ou une sous-couche.

6. Le support selon les revendications 1—4, caractérisé en ce que sa surface porte un film, d'oxydation anodique et une sous-couche.

7. Le support selon la revendication 5 ou 6, caractérisé en ce que la sous-couche est constituée d'une cellulose hydrophile contenant un sel métallique hydrosoluble.

8. Le support selon les revendications 1—7, caractérisé en ce que la surface dudit matériau en alliage d'aluminium forme un plan rugueux ayant des creux primaires de 0,3 à 1,2 μm (exprimé en Ra) dans une rugosité moyenne de 1 à 10 μm de profondeur moyenne.

9. Le support selon les revendications 1—7, caractérisé en ce que la surface dudit matériau en alliage d'aluminium forme un plan rugueux ayant des creux secondaires de 1 μm ou moins de profondeur moyenne et 5 μm ou moins de diamètre d'ouverture moyen.

10. Plaque d'impression lithographique photosensible, caractérisée en ce qu'elle comprend un support selon les revendications 1—9, portant une couche photosensible.

11. La plaque d'impression lithographique photosensible selon la revendication 10, caractérisée en ce que la couche photosensible est présente en une quantité de l'ordre de 0,1 à 7 g/m^2 .

12. La plaque d'impression lithographique photosensible selon la revendication 11, caractérisée en ce que la couche photosensible est présente en une quantité de l'ordre de 0,5 à 4 g/m^2 .

13. Procédé de production de support pour plaque d'impression lithographique selon les revendications 1—9, caractérisé par les étapes consistant à:

a) obtenir un matériau en alliage d'aluminium selon la revendication 1;

b) soumettre une surface du matériau en alliage d'aluminium à un décapage chimique par une solution d'un acide ou d'un alcali; et

c) soumettre la surface à un traitement de décapage électrochimique dans une solution électrolytique acide.

14. Procédé de production de plaque d'impression lithographique photosensible selon les revendications 10—12, caractérisé en ce qu'il consiste à:

a) obtenir un matériau en alliage d'aluminium selon la revendication 1;

b) soumettre une surface du matériau en alliage d'aluminium à un décapage chimique par une solution d'une acide ou d'un alcali;

c) soumettre la surface à un traitement de décapage électrochimique dans une solution électrolytique acide; et

d) appliquer une couche photosensible sur la structure granulaire uniforme et dense de la surface.

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