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(54) Aluminium alloy, a support of lithographic printing plate and a lithographic printing plate using the same.

(57) An aluminium alloy, a lithographic printing plate support, a lithographic printing plate and a process for producing it are disclosed. The plate support is produced by providing an aluminium alloy material which is comprised of 0.20 to 1.0% Fe, 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga and Zn and the remainder being aluminium. The alloy may further contain 0.1 to 2% Cu and/or 0.1 to 0.6% Mg. After providing the aluminium material either or both of its surfaces are sujected to a chemical etching treatment in order to provide a uniform and dense grain structure on the surface forming primary pits in the surface having a particularly defined average size. The surface is then optionally subjected to electrochemical etching treatment in an acidic electrolitic solution in order to provide secondary pits on the surface also having a particularly defined average size. The support base may be further treated to provide in additional coating thereon or directly coated with a light-sensitive layer in order to provide a light-sensitive lithographic printing plate. By providing the particular alloy material and subjecting it to the disclosed treatment the light-sensitive layer has good adhesion with respect to the support.

Croydon Printing Company Ltd.

ALUMINUM ALLOY, A SUPPORT OF LITHOGRAPHIC PRINTING PLATE AND A LITHOGRAPHIC PRINTING PLATE USING THE SAME

FIELD OF THE INVENTION

The present invention relates to an aluminum alloy, a lithographic printing plate support and a lithographic printing plate using the same.

BACKGROUND OF THE INVENTION

In 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 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 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.

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.

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 μRa (centerline 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 harmful for workers, thus causing a problem in view of working atmosphere. (3) The etching cost is too high to be practical.

SUMMARY OF THE INVENTION

The present invention relates to an aluminum alloy, a lithographic printing plate support and a lithographic printing plate using the aluminum alloy which solve the above-described problems.

Accordingly, an object of the present invention is to provide an aluminum alloy, 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 the same which is suited for printing.

Thus, the present invention relates to:

i) An aluminum alloy, which contains 0.20 to 1.0% Fe and 0.005 to 0.1% of at least one element selected from among Sn, In, Ga, and Zn,

ii) An aluminum alloy, which contains 0.20% to 1.0% Fe, 0.005 to 0.1% of at least one element selected from among Sn, In, Ga, and Zn, and 0.1 to 2% Cu and/or 0.1 to 0.6% Mg,

iii) A support for a lithographic printing plate comprising the aluminum alloy described in the above items (i) and (ii),

iv) A support for a lithographic printing plate described in the above item (iii), the support having an etched surface, i.e., chemical etched surface or chemical etched and electrochemical etched surface,

v) A lithographic printing plate comprising the supprot described in item (iv) and a light-sensitive layer provided thereon, and processes producing them.

DETAILED DESCRIPTION OF THE INVENTION

The aluminum alloy of 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.

The alloy composition in accordance with 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 expressed by weightunless otherwise stated.) If the content of Fe and Cu and/or Mg are more than is 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, Ga and Zn 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 microns at most, which means that the pit pattern must be fine.

It has been surprisingly found that addition of small amounts of Sn, In, Ga or Zn series element 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% and particularly 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 serious, making it difficult to form a uniform pit pattern.

The aluminum alloy of 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, Ga and Zn, 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 comprised of the alloy of the present invention is subjected to at least one chemical etching step and optionally followed by electrochemical etching step.

The chemical etching of the aluminum alloy is carried out using an acid or alkali such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, etc., or a mixture of two or more of these acids, and sodium hydroxide, sodium carbonate, sodium tertiary phosphate, sodium silicate, etc., are used as the alkali. Concentration and temperature of the etching solution depend upon 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 seconds to about 4 minutes. 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. 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 μ, which corresponds to an average roughness of 0.3 to 1.2 μm (presented as Ra) and an opening diameter of 1 to 10 μ.

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 a uniform etching pit pattern wherein the pits have a uniform diameter and a 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 second to 10 minutes, preferably 3 seconds to 5 minutes. 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, etc., 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 conditons 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 ampere/dm^2, a voltage applied of 1 to 100 v and an electrolyzing time of 10 to 100 seconds 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, etc.) containing a water-soluble metal salt (e.g., zinc acetate, etc.) and ranged in preferable thickness of 0.001 to 1 g/m^2, more preferable 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).

On the lithographic printing plate support prepared in accordance with an embodiment of the present invention, a light-sensitive layer which is known to have been used for presentitized plates is provided 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-solution 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 so on, and compositions comprised of 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, and so on.

The amount (thickness) of the light-sensitive layer to be provided on the support is controlled to about 0.1 to about 7 g/m^2, preferably 0.5 to 4 g/m^2.

Lithographic printing plates, after imagewise exposure, are subjected to processings 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.

However, the scope of the invention is not limited to these 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 fluorescene 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 No.		Alloy Composition (weight %)							
		Aℓ	Fe	Cu	Mg	Sn	In	Ga	Zn
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	98.55	0.70	0.50	-	0.05	-	-	0.20
	5	99.75	0.20	-	-	0.05	-	-	-
	6	99.06	0.30	0.60	-	0.04	-	-	-
	7	99.26	0.70	-	-	0.04	-	-	-
	8	99.10	0.85	-	-	0.05			
	9	98.70	0.85	-	0.20	0.05	-	-	0.20
	10	98.71	0.83	-	0.25	-	0.06	-	0.15
	11	98.77	0.35	-	9.55	-	-	0.03	0.30
	12	98.91	0.83	-	0.21	0.05	-	-	-
	13	98.25	0.70	0.52	0.26	0.05	-	-	0.22

EXAMPLE 2

The following aluminum alloy plates were prepared and subjected to a chemical graining treatment for 1 minute 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/m²	Surface Roughness μm	Surface Appearance Opening Diameter
Comparison 1'A	26	0.37	non-uniform pit pattern, coarse pits of 7 to 15 μ
2'A	27	0.34	Same as above
3'A	21	0.19	uniform pit pattern, slightly coarse pits of 2 to 8 μ
Present Invention 1 A	27	0.35	uniform pit pattern 2 to 8 μ pits
2 A	27	0.33	Same as above
3 A	26	0.30	"
4 A	28	0.37	"
5 A	23	0.30	"
6 A	24	0.37	"
7 A	27	0.34	"
8 A	28	0.34	"
9 A	27	0.51	"
10 A	27	0.47	"
11 A	21	0.45	"
12 A	21	0.51	"
13 A	28	0.50	"

As is apparent from the Table 2, Sample Nos. 9A to 13A containing Fe and Mg as a main component have pit patterns having 2 to 8 μ of opening diameter and 0.45 μm or more of average surface roughness.

On the other hand, Sample Nos. 1A to 8A which contain Cu but contain no Mg have uniform pit patterns having 2 to 8 μ of pit diameter. Those samples have a considerably good surface-appearance in comparison with Comparative Samples. Values of average surface roughness is slightly low in comparison with Samples containing Mg.

Then, Sample Nos. 1'A, 2'A and 3'A and Sample Nos. 1 to 4A and 6A to 13A were subjected to an electrochemical etching treatment in a 7 g/liter nitric acid aqueous solution in an electricity amount of 100 coulomb/dm^2 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% H_2SO_4 aqueous solution at 55°C for 1 minute. Subsequently, a 3 g/m^2 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 minute, thoroughly washing with water, and drying.

Surface roughness of each of the thus-obtained samples was determined, and their pit patterns were 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	1 ∿ 3
	2B	0.34	"	"
	3B	0.32	"	"
	4B	0.37	"	"
	6B	0.38	"	"
	7B	0.37	"	"
	8B	0.37	"	"
	9B	0.51	"	"
	10B	0.48	"	"
	11B	0.46	"	"
	12B	0.51	"	"
	13B	0.50	"	"
Comparison	1'B	0.38	"	"
	2'B	0.36	"	"
	3'B	0.20	"	"

Sample Nos. 1B to 13B 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. 7A, 7B, 10A and 10B and Comparative Sample No. 3'B obtained in Example 1 was coated the following light-sensitive layer in a dry thickness of 2.0 g/m^2.

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 seconds by means of a metal halide lamp of 3 kw placed at a distance of 1 meter, and dipped in the following developing solution for 1 minute 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.

<u>Formulation of Developing Solution</u>:

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

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

Table 4

Plate	7A	7B	10A	10B	3'B
Support	7A	7B	10A	10B	3'B
Primary pits:					
Average Depth (μm)	1 ∿ 10	1 ∿ 10	1 ∿ 10	1 ∿ 10	1 ∿ 6
Opening Diameter (μm)	2 ∿ 8	2 ∿ 8	2 ∿ 8	2 ∿ 8	2 ∿ 8
Secondary pits:					
Average Depth (μm)	—	0.1 ∿ 0.8	—	0.1 ∿ 0.8	0.1 ∿ 0.8
Opening Diameter (μm)	—	1 ∿ 3	—	1 ∿ 3	1 ∿ 3
Amount of Electrochemically Etching Electricity (C/dm^2)	—	100	—	100	100
Weight of Anode Oxidation Film (g/m^2)	3.0	3.0	3.0	3.0	3.0
Surface Roughness (μm)	0.34	0.37	0.47	0.48	0.19
Printing Durability	80,000	130,000	90,000	150,000	100,000
Staining Resistance	excellent	excellent	excellent	excellent	fair

As is apparent from Table 4, plates of Nos. 7B, and 10B having supports of Nos. 7B and 10B respectively which were subjected to electrochemical etching treatment were extraordinary improved in printing durability in comparison with plates of Nos. 7A and 10A having supports of Nos. 7A and 10A which were not treated. Further, the plates of Nos. 7B and 10B were superior to the plate No. 3'B wherein the support is subjected to electrochemical etching. Because, it seems that the support of No. 3'B has a lower value in surface roughness.

The plates of Nos. 10A and 10B are superior in printing durability to those of Nos. 7A and 10A.

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 minutes, then to a second chemical graining treatment in an aqueous mixture solution of 300 ml/liter nitric acid and 150 m./liter 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

Sample	Time for First Treatment	Surface Roughness (uRa)	Pit Pattern
$1C_1$	1 min.	0.40	uniform, mixed pattern of 2 - 8 μ pits and 0.1 - 0.3 μ 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	"
Comparative Ex.			
$2'C_5$	5 min.	0.57	non-uniform, 10 - 19 μ coarse pits
$3'C_5$	5 min.	0.73	uniform

A plane with a large surface roughness was formed on sample Nos. $1C_1$ to $1C_5$ due to its large solution quantity for both acid and alkali. In addition, sample Nos. $1C_1$ to $1C_5$ had a multi pit pattern wherein uniform 1 to 5 μ pits were formed with acid in uniform 2 μ to 8-μ-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. $1C_5$ 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 3 g/m^2 oxide film, then dipped in a 2.5% aqueous solution of sodium silicate (JIS No.3) at 60°C for 1 minute, washed throughly with water, and dried.

The thus-treated samples prepared from sample No. 1A, comparative samples Nos. 2'A and 3'A, and sample No. $1C_5$ were referred to as sample Nos. (1A), (2'A), (3'A) and ($1C_5$)D, respectively. On each of the thus-prepared samples was coated the solution used in Example 3 in a dry thickness of 2.0 g/m^2 to prepare lithographic printing plates.

The thus-obtained light-sensitive lithographic printing plates were each imagewise exposed for 70 seconds by means of a metal halide lamp of 3 kw placed at a distance of 1 meter, 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 ($1C_5$)D were obtained, respectively.

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

Table 6

Sample	(1A)	(2'A)	(3'A)	$(1C_5)D$
Support	(1A)	(2'A)	(3'A)	$(1C_5)D$
Surface Roughness (Ra)	0.35 μ	0.34 μ	0.19 μ	0.51 μ
Degree of Uniformity of Pits	uniform, 2-8 μ pits	coarse, 7-15 μ pits (non-uniform)	uniform, 2-8 μ pits	mixture pattern of uniform 2-8 μ pits and 1-5 μ pits
Printing Durability	80,000	50,000	20,000	100,000
Staining Resistance	excellent	fair	excellent	excellent

EXAMPLE 6

Sample Nos. 9A and 8A, 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 3 g/m^2 oxide film, then dipped in a 2.5% aqueous solution of sodium silicate (JIS No.3) at 60°C for 1 minute, washed throughly with water and dried.

The sample Nos. 9A and 8A thus treated and Comparative sample No.1 were referred to as Support Nos. (9A)E, (8A)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.

The lithographic printing platesthus obtained were each imagewise exposed for 70 seconds by means of a metal halide lamp of 3 KW placed at a distance of 1 meter, and dipped in the developing solution shown in Example 3 for 1 minute at room temperature. Then, the surface of each plate was lightly rubbed by an absorbent wadding, to remove unexposed areas, thus printing platesNos. (9A)E, (8A)E and (1'A)E were obtained, respectively.

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

Table 7

Sample	(9A)E	(8A)E	(1'A)E
Support	(9A)E	(8A)E	(1'A)E
Surface Roughness (Ra)	0.51 μm	0.34 μm	0.37 μm
Degree of Uniformity of Pits	uniform 2 to 8 μm pits	uniform 2 to 8 μm pits	non-uniform 7 to 15 μm coarse pits
Printing Durability	90,000 (sheets)	70,000	50,000
Staining Resistance	excellent	excellent	fair

Sample Nos. (9A)E and (8A)E are superior to Sample No. (1'A)E in printing durability and staining resistance, and further Sample No. (9A)E is excellent in comprarison with Sample Nos. (8A)E and (1'A)E due to a larger average surface roughness of Sample No. (9A)E.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the sprit and the scope thereof.

WHAT IS CLAIMED IS:

1. An aluminum alloy, which contains 0.20 to 1.0% Fe and 0.005 to 0.1% of at least one element selected from among Sn, In, Ga, and Zn.

2. An aluminum alloy, which contains 0.20% to 1.0% Fe, 0.005 to 0.1% of at least one element selected from among Sn, In, Ga, and Zn, and 0.1 to 2% Cu and/or 0.1 to 0.6% Mg.

3. A support for a lithographic printing plate, comprising an aluminum alloy material containing 0.20 to 1.0% Fe and 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga and Zn.

4. A support for a lithographic printing plate as claimed in Claim 3, further comprising 0.1 to 2% Cu and/or 0.1 to 0.6 % Mg.

5. A support for a lithographic printing plate as claimed in Claim 3, wherein a surface of the support is chemically etched.

6. A support for a lithographic printing plate as claimed in Claim 5, wherein the surface is chemically etched with an etching solution of an acid selected from the group of acids consisting of hydrochloric acid, nitric

acid, sulfuric acid, phosphoric acid, and hydrofluoric acid or an alkali solution selected from of the group of alkalis consisting of sodium hydroxide, sodium carbonate, sodium tertiary phosphate and sodium silicate.

7. A support for a lithographic printing plate as claimed in Claim 5, wherein the surface of the support has an anode oxidation film provided thereon.

8. A support for a lithographic printing plate as claimed in Claim 5, wherein the surface has provided thereon a subbing layer.

9. A support for a lithographic printing plate as claimed in Claim 8, wherein the subbing layer is comprised of a hydrophilic cellulose containing a water-soluble metal salt.

10. A lithographic printing plate, comprising;

a printing plate support comprised of 0.20 to 1.0% Fe, 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga and Zn, and the remainder being Al, the support having an etched surface; and

a light-sensitive layer provided on the etched surface.

11. An aluminum alloy lithographic printing plate as claimed in Claim 10, wherein the light-sensitive layer is present in an amount within the range of 0.1 to 7 g/m^2.

12. An aluminum alloy lithographic printing plate as claimed in Claim 11, wherein the light-sensitive layer is present in an amount within the range of 0.5 to 4 g/m^2.

13. A support for a lithographic printing plate, which comprises an aluminum alloy material containing 0.20 to 1.0% Fe and 0.005 to 0.1% of one, two or more of Sn, In, Ga, and Zn and having at least on one surface thereof a uniform and dense grain structure formed by subjecting its surface to a chemical etching treatment and then to an electrochemical etching treatment in an acidic electrolytic solution.

14. A support for a lithographic printing plate as described in Claim 13, wherein said aluminum alloy material further contains 0.1 to 2% Cu and/or 0.1 to 0.6% Mg.

15. A support for a lithographic printing plate as described in Claim 13, wherein 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 formed by the chemical etching treatment.

16. A support for a lithographic printing plate as described in Claim 13, wherein 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 formed by the electrochemical treatment.

17. A light-sensitive lithographic printing plate, which comprises a support having provided thereon a light-sensitive layer, said support comprising an aluminum alloy material containing 0.20 to 1.0% Fe and 0.005 to 0.1% of one, two or more of Sn, In, Ga, and Zn and having at least on one surface thereof a uniform and dense grain structure formed by subjecting its surface to a chemical etching treatment and then to an electrochemical etching treatment.

18. A method for producing a lithographic printing plate support, comprising the steps of:

providing an aluminum alloy material comprised of 0.20 to 1.0% Fe, 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga, and Zn, and the remainder being aluminum;

subjecting a surface of the aluminum alloy material to a chemical etching treatment in order to form uniform and dense grain structure on the surface;

subjecting the surface to electrochemical etching treatment in an acidic electrolytic solution.

19. A method for producing a lithographic printing plate support as claimed in Claim 18, wherein the aluminum alloy material is further comprised of 0.1 to 2% Cu. and/or 0.1 to 0.6 % Mg.

20. A method for producing a lithographic printing plate support as claimed in Claim 19, wherein the chemical etching treatment provides pits in the surface so that the surface has an average roughness (Ra) in the range of 0.3 to 1.2 μm and the pits formed in the surface have an average depth of 1 to 10 μm.

21. A method for producing a lithographic printing plate support as claimed in Claim 19, wherein the electrochemical treatment forms secondary pits in the surface having an average depth of 1 μm or less and an average diameter of 5 μm or less.

22. A lithographic printing plate support, produced by the process comprising the steps of:

providing an aluminum alloy material comprised of 0.2 to 1.0% Fe, 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga and Zn and the remainder being aluminum;

subjecting a surface of the aluminum alloy material to a chemical etching treatment in order to form a uniform and dense grain structure on the surface; and

subjecting the surface to an electrochemical etching treatment in an acidic electrolytic solution.

23. A lithographic printing plate support produced by the process as claimed in Claim 22, wherein the aluminum alloy material is further comprised of 0.1 to 2% Cu and/or 0.1 to 0.6% Mg, the chamical etching treatment provides primary pits having an average diameter of 0.3 to 1.2 µm and an average depth of 1 to 10 µm, and the electrochemical treatment provides secondary pits having an average depth of 1 µm or less and an average diameter of 5 µm or less.

24. A method for producing a light-sensitive lithographic printing plate, comprising the steps of:

providing an aluminum alloy material comprised of 0.20 to 1.0% Fe, 0.005 to 0.1% of an element selected from the group consisting of Sn, In, Ga, and Zn, 0.1 to 2% Cu and the remainder being aluminum;

subjecting a surface of the aluminum alloy material to a chemical etching treatment in order to form a uniform and dense grain structure on the surface with primary pits having an average diameter of 0.3 to 1.2 μm and an average depth of 1 to 10 μm;

subjecting the surface to an electrochemical etching treatment in an acidic electrolitic solution to provide secondary pits having an average depth of 1 μm or less and an average diameter of 5 μm or less; and

providing a light-sensitive layer on the uniform and dense grain structure in the surface

25. A method for producing a light-sensitive lithographic printing plate as claimed in Claim 24, wherein the light-sensitive layer is present in an amount within the range of 0.1 to about 7 g/m^2.

26. A method for producing a light-sensitive lithographic printing plate as claimed in Claim 25, wherein the light-sensitive layer is present in an amount within the range of 0.5 to 4 g/m^2.