

SUPPORTS FOR LITHOGRAPHIC PRINTING PLATES

The present invention relates to aluminium supports for lithographic printing plates.

In order to use aluminium plates as supports for lithographic printing plates, the surface is generally roughened to improve adhesion to a sensitive layer provided thereon and to improve the water retention property. The treatment for roughening the surface is called graining, and mechanical graining such as ball graining, wire graining and brush graining, and electrochemical graining, i.e., electrolytic etching are known.

Since the aluminium surface grained by these processes is comparatively soft and easily abraded, it is then subjected to anodic oxidation to form an oxide film thereon. The resulting surface of the processed aluminium plate is hard and exhibits excellent abrasion resistance, good affinity for water, good water retention and good adhesion to the photosensitive layer. However, when anodic oxidation alone is carried out directly after the mechanical graining, the oxide film is blackened by insoluble substances (for example, the remnants of abrasives, aluminium cutting dusts or brush fragments) formed during graining treatment and, consequently, the appearance is damaged. Further, the sensitivity of a sensitive layer applied thereto deteriorates or becomes uneven, the visual contrast

between the image and the non-image areas is poor even with development and, consequently, further operations are indispensable for plate making, such as correction or elimination. However, not only operations in printing, 5 for example, control of water/ink balance, become difficult, but also the non-image area is easily contaminated. For this reason an intermediate treatment is generally carried out after graining and before anodic oxidation. As the intermediate treatment, a chemical 10 etching process is described in U.S. Patent 3,834,998 and an electrochemical etching process is described in U.S. Patent 3,929,591. In the case of electrochemical etching, though the treated surface is somewhat white compared with the aluminium surface subjected to graining 15 and then anodic oxidation, halation does not substantially occur but the sensitivity is low and interferes with post-development operations such as correction or elimination of images. Further, printing operations (e.g., adjustment of balance between water and ink) become 20 difficult to accomplish.

In the case of chemical etching, though contamination of the non-image area and resistance to scratching are improved, a fine grain structure formed on the aluminium surface is broken. Therefore, the excellent 25 surface characteristics of the graining treatment deteriorate, water retention and printing durability become inferior and fine halftone dots of 1 to 5% cannot

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be reproduced.

Accordingly, an object of the present invention is to provide supports for lithographic printing plates having excellent affinity for water, good water retention
5 properties and improved printing durability, and which can be used to form photosensitive lithographic printing plates having high sensitivity and excellent plate inspection properties.

As a result of extensive studies directed to attain-
10 ing the above-described object, it has been found that the micro-structure of the fine uneven surface observed on an aluminium support when magnified, for example, 2,000 to 5,000 times, has a very large influence on the qualities of the plate as a support for a
15 lithographic printing plate.

According to the present invention we provide a support for a lithographic printing plate comprising an aluminium sheet, the surface of which has a grain structure as observed in enlargement of 2,000 times by a
20 scanning electron microscope, comprising mounds, and pits each having a defined opening, which uniformly pierce the surface of said mounds, in a direction nearly perpendicular to the surface of the mound, and the pits are present in such a sparse uniform density that ^{face of the} the mounds ^{is} are still apparent.

25 Preferably the distribution of pit diameter is such than the pits corresponding to 5% and 95% on a cumulative frequency curve for pit diameter have a diameter of 3μ or less, and 7μ or less, respectively.

The present invention and its background will now be discussed with reference to the accompanying drawings, in which:

Figure 1 (a) is a photograph of the surface of aluminium plate grained by brush graining process, which is enlarged 2,000 times by a scanning electron microscope, and Figure 1 (b) is a cross-sectional representation of this surface. It is understood from Figure 1 (b) that the surface of the aluminium plate roughened by brush graining is a continuous wave composed of hills and valleys having various cycles and amplitudes. In the figure, the wave having the comparatively long cycle is called a primary structure and the wave having a short cycle is called a secondary structure. A feature of the rough surface of a brush-grained aluminium plate is that the secondary structure is formed on the primary structure in such a density that the face of the primary structure itself does not remain. (The term "face of the primary structure" refers to what would be the unpitted undulations in Figure 1 (b).) Moreover, the direction with which the pits in the secondary structure pierce the primary structure is random and the pits have a complicated two- or three-dimensional arrangement, though this cannot be shown in the two dimensions in Figure 1 (b). The pits do not have rounded openings (as in Fig. 3 (b)). Such a complicated secondary structure is a predominant feature of the rough surface of the mechanically grained aluminium plate. Accordingly, since the surface has such

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a complicated structure, supports for lithographic printing plates resulting from anodic oxidation of this surface have the above-described faults.

Figure 2 (a) is a photograph of the surface of an aluminium plate which was chemically etched after mechanical graining enlarged 2,000 times by a scanning electron microscope. Figure 2 (b) is a cross-sectional representation of the surface. As shown in Figure 2 (b), the secondary structure in the surface of the mechanically grained aluminium plate disappears and a gently-sloping undulation (hereinafter, referred to as a mound) is formed.

The aluminium plate which is subjected to chemical etching after mechanical graining has a surface having high whiteness upon anodic oxidation, and a lithographic printing plate with little contamination of non-image areas can be obtained. However, since the secondary structure disappears, image portions on the lithographic printing plate easily peel from the surface of the support under the physical forces of printing and, consequently, the printing durability deteriorates.

Figure 3 (a) is a photograph of the surface of an aluminium plate which was subjected to electrolytic etching treatment after first mechanical graining then chemical etching treatments, enlarged 2,000 times by a scanning electron microscope. Figure 3 (b) is a cross-sectional representation of the surface. As is obvious from Figures 3 (a) and (b), a new secondary structure is

formed in place of the secondary structure formed by mechanical graining on the surface of the aluminium plate in which the primary structure formed upon chemical etching after mechanical graining predominates. This new secondary structure is remarkably different from the above-described secondary structure (i.e., the secondary structure formed by mechanical graining), because the direction with which the pits pierce the mount face is nearly perpendicular thereto and the pits are comparatively sparsely dispersed, namely, occur with such a frequency that the mounds remain though the pits are uniformly present, and as seen in Fig. 3(a) the pits generally have a definite circular or rounded opening.

Since the aluminium plate having the secondary structure shown in Figures 3 (a) and (b) has high whiteness upon anodic oxidation, a photosensitive lithographic printing plate having a sensitive layer provided thereon provides high sensitivity, and a lithographic printing plate obtained therefrom has the advantage that presence of unnecessary image areas can be easily distinguished by the high contrast between the image areas and non-image areas. Further, this lithographic printing plate has high printing durability, because the image areas do not peel off during printing due to the pits making up the secondary structure. Further, since the pits composing the secondary structure are dispersed at such a density that the mounds remain, a lithographic printing plate having little contamination in the non-image areas is

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produced. Further, the fact that the piercing direction of pits composing the secondary structure is simple as compared with the case of the secondary structure formed by mechanical graining is one of the reasons the lithographic printing plate having little contamination as described above can be produced.

This electrochemical graining is preferably carried out so that the pore diameters corresponding to 5% and 95% pore diameter on the cumulative frequency curve of the grain formed are respectively $3\ \mu$ or less, preferably 0.5 to $3\ \mu$ and $7\ \mu$ or less, preferably 5 to $7\ \mu$. Further, the preferred density of the pits is 10^6 to 10^8 pits/cm².

In spite of the recognition that an aluminium plate with a grain falling within the above range provided on the surface thereof is, as described in British Patent Publication No. 2,019,022 A, not suitable for use as a support for a lithographic printing plate, it has now surprisingly been found that the aluminium plate with such a grain, which can be produced by a combination of mechanical graining and electrochemical graining, is usable as an excellent support for the lithographic printing plate. Additionally, since the formation of the surface with such a grain by electrochemical graining is relatively easy, the process is markedly advantageous from the standpoint of production.

The above pore diameter cumulative frequency curve can be obtained by magnifying the surface of a piece of the electrochemically grained aluminium plate 100 to 700 times by the use of a scanning type electron microscope, 5 for example, measuring the diameters and number of pores in a unit area, and then plotting the pore diameter (μ) as the abscissa and the cumulative frequency (%) as the ordinate.

A process for producing supports for lithographic 10 printing plates according to the present invention will now be described in detail.

The aluminium plate used in the present invention includes pure aluminium plates and aluminium alloy plates. As aluminium alloys, various alloys can be used. For 15 example, there are alloys of aluminium and metals such as silicon, copper, manganese, magnesium, chromium, zinc, lead, bismuth or nickel. These compositions may contain impurities in amounts which can be disregarded in addition to some iron and titanium.

20 Specific examples of the suitable aluminium alloys are set forth in the following Table below wherein all numerical figures are in terms of percent by weight.

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Al Alloy No.	Cu	Si	Fe	Mn	Mg	Zn	Cr	Ti	Al
1050*	0.05	0.25	0.40	0.05	0.05	0.05	--	0.03	>99.5
1100*	0.05-0.20	1.0	1.0	0.05	--	0.10	--	--	>99.0
3003	0.05-0.20	0.6	0.7	1.0-1.5	--	0.10	--	--	balance
2024	3.8-4.9	0.5	0.5	0.3-0.9	1.2-1.8	0.25	0.10	--	balance
5052	0.10	0.45	0.45	0.10	2.2-2.8	0.10	0.15-0.35	--	balance
6061	0.15-0.40	0.40-0.8	0.7	0.15	0.8-1.2	0.25	0.04-0.35	0.15	balance
7075	1.2-2.0	0.40	0.5	0.30	2.1-2.9	5.1-6.1	0.18-0.35	0.20	balance

* The amounts other than that of Al show maximum.

Prior to mechanical graining, the aluminium surface is generally de-greased and the aluminium surface is treated in order to expose a clean aluminium surface. For the former purpose, solvents such as trichloroethylene, and surface active agents are used. For the latter purpose, an alkali etching process using agents such as sodium hydroxide or potassium hydroxide has been widely used. Unless the rolling oil adheres strongly, the de-greasing treatment prior to mechanical graining can be omitted.

It is possible to use electrochemical graining (electrolytic etching) which comprises graining by sending an electric current through an electrolyte comprising hydrochloric acid or nitric acid, mechanical graining processes such as wire-brush graining which comprises scratching the aluminium surface with metal wires, ball graining which comprises graining the aluminium surface with abrasive balls and abrasives, or brush graining which comprises graining the surface with a nylon brush. However, a brush graining process is preferred because it is suitable for continuous mass production. However, the surface structure which is a characteristic of the present invention cannot be obtained by utilizing any of the above-described processes for graining or combinations thereof alone. The grained surface consists of a fine structure (secondary structure) which is smoothed by chemical etching and a roughened face (primary structure) which is not

destroyed by the chemical etching.

Among these procedures, the brush graining is particularly preferred. Details of the brush graining are described in Japanese Patent Publication No. 40047/75 and
5 U.S. Patent 3,891,516.

The graining is preferably carried out so that the center line average roughness (Ra) of the support is 0.4 to 1.0 μ . The center line average roughness as herein used is, as illustrated in JIS-B 0601-1970, given in microns
10 by the following equation:

$$Ra = \frac{1}{L} \int_0^L f(x) dx$$

wherein l is a length taken from the roughness curve in the direction of the center line, and $y=f(x)$ is the roughness curve with the center line of the length taken as the
15 X axis and the longitudinal direction taken as the Y axis.

The degree of the mechanical graining to provide the above defined Ra range can be easily determined by one skilled in the art when the conditions of the electro-chemical graining to be applied subsequently and of other
20 additional processings to be applied as necessary are determined.

The aluminium plate subjected to graining treatment is then chemically etched with an acid or an alkali. In the case of using the acid as an etching agent, a very long
25 period of time is required to destroy the fine structure

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and, consequently, it is industrially disadvantageous for making a plate of the invention. The process can be improved by using alkali as the etching agent.

As the alkali agent suitable used in the present invention, there are sodium hydroxide, sodium carbonate, sodium aluminate, sodium metaborate, sodium phosphate, potassium hydroxide and lithium hydroxide. Preferable concentration and temperature ranges are 1 to 50% by weight and 20 to 100°C, respectively, and it is particularly preferred to use a condition that dissolves Al in an amount of 5 to 20 g/m². By etching 5 g/m² or more of the Al, a rough face consisting of the primary structure itself, namely, mounds can be formed.

After etching, acid washing is carried out in order to remove smut on the surface. As the acid, nitric acid, sulfuric acid, phosphoric acid, chromic acid, hydrofluoric acid or borofluoric acid are used.

The aluminium plate treated as described above is then subjected to electrolytic etching in order to form a new secondary structure. This treatment is carried out by electrolyzing the plate in an acid aqueous solution of, for example, hydrochloric acid, nitric acid or a mixture thereof, with 200 coulombs/dm² or less of electricity being supplied at a current density not less than 20 A/dm² while the plate is an anode using a suitable counter electrode such as a graphite or aluminium plate, so that the quantity of electricity with the plate as an anode



(referred to as Q_a hereinafter) is equal to or greater than the quantity of electricity with the plate as a cathode (referred to as Q_c hereinafter).

The alternative wave-form electric current used in the present invention is a wave-form obtained by alternately changing the polarity of positive and negative electrodes, and any wave-form may be used as long as Q_a is equal to or greater than Q_c . A preferred voltage wave-form giving such a current waveform is one in which the anodic voltage (V_a) is larger than the cathodic voltage (V_c). Figure 4 shows typical voltage wave-forms among preferred voltage wave-forms, wherein (a) is a sine wave, (b) is a rectangular wave and (c) is a trapesoidal wave. In these cases, it is preferred to set the anodic half-cycle period (Figure 4, t_A) so that it is equal to or less than the cathodic half-cycle period (Figure 4, t_C). By changing the ratio Q_c/Q_a by regulating the voltage and the current density, the micro-structure of the porous surface (the diameter and density of pits) can be suitably controlled. Further, when " V_a " is constant and " V_c " increases, the diameter of the pits tend to increase. Conversely, when " V_c " is constant and " V_a " increases, the diameter of the pits tend to decrease. The pit diameter also tends to increase as the temperature of the treatment increases or the current density increases. It is thus possible to produce a grained surface whose pore diameters corresponding to 5% and 95% of the pore density cumulative

frequency curve of the grain formed are respectively 3 μ or less and 7 μ or less.

In the present invention, it is necessary to carry out the above-described electrolytic treatment in such a manner that the pits are uniformly dispersed on the above-described mounds but the mounds (primary structure) remain.

If the pits are formed over the entire surface so that the mounds disappear, the characteristic that non-image areas are difficult to soil is lost. If the pits are not uniformly distributed or they are formed in local gatherings, it becomes difficult to obtain suitable printing durability and tonal reproduction.

As the electrolytic bath, a solution of one or more of hydrochloric acid or salts thereof and nitric acid or salts thereof may be used. If necessary, inhibitors and stabilizers such as amines described in U.S. Patent 3,755,116, sulfuric acid described in U.S. Patent 3,980,539, boric acid described in Japanese Patent Application (OPI) No. 41653/76 (the term "OPI" as used herein refers to a "published unexamined Japanese Patent Application") and phosphoric acid described in German Patent Application (OLS) No. 2250275, may be added to the above-described solution.

The electrolyte can be used at a concentration of about 0.1 to 4% by weight. Further, values of V_a and V_c suitable for producing the desired grain structure are both in the range of about 1 to 50 V and preferably about 5 to 30 V. Further, each of Q_a and Q_c is in the range of

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200 coulombs/dm² or less and preferably about 70 to 200 coulombs/dm². If it is more than 200 coulombs/dm², contamination of the non-image areas is difficult to prevent. The temperature of the treatment is usually between about 5 10°C and about 45°C, preferably about 15 to 45°C.

In order to uniformly disperse the pits, the ratio Q_c/Q_a is preferably in the range of about 0.5/1 to 1.0/1 and more preferably about 0.7/1 to 0.95/1. It is necessary that the anodic current density upon electrolysis is about 20 A/dm² or more and preferably about 10 25 to 70 A/dm². If the anodic current density is less than about 20 A/dm² and the quantity of anodic electricity is less than 200 coulombs/dm², it is difficult to maintain adequate printing durability, water retention and the reproduction of fine halftone dots. 15

The aluminium plate treated as described above can be used as a support for lithographic printing plates as is, but it may be further processed by anodic oxidation treatment or chemical treatment.

20 The anodic oxidation treatment may be carried out just after water wash of the aluminium plate treated as described above, but it is preferred to carry out desmutting in order to remove the smut, which forms on the surface of the electrolytically treated aluminium plate. Desmutting is carried out by contacting the 25 surface of the aluminium plate with an aqueous solution of acid or alkali by, for example, dipping. Examples of the acids include phosphoric acid, sulfuric acid and

chromic acids and mixtures thereof. As the alkali, it is possible to use the same substances as used in the chemical etching after mechanical roughening treatment. Among them, a particularly preferred desmutting process
5 comprises contacting the support with sulfuric acid at a concentration of about 15 to 65% by weight at 50 to 90°C as described in Japanese Patent Application (OPT) No. 12739/78. The alkali etching process described in Japanese Patent Publication No. 28123/73 can also be
10 used.

Anodic oxidation can be carried out by a known process. For example, it is possible to form an anodic oxidation film on the surface of the aluminium plate by applying a direct current or an alternating current to
15 the aluminium plate in an aqueous solution or a non-aqueous solution of one or more of sulfuric acid, phosphoric acid, chromic acid, oxalic acid, sulfamic acid and benzenesulfonic acid.

Though the conditions vary according to the
20 electrolyte used, it is generally preferred that the concentration of the electrolyte is about 1 to 30% by weight, the liquid temperature is about 5 to 70°C, the current density is about 0.5 to 60 amperes/dm², the voltage is about 1 to 100 V and the electrolysis time is
25 about 30 seconds to 50 minutes.

As the anodic oxidation treatment, it is particularly preferred to use a process which comprises carrying out anodic oxidation in sulfuric acid at a high

current density described in British Patent 1,412,768 and a process which comprises carrying out anodic oxidation using phosphoric acid as an electrolytic bath as described in U.S. Patent 3,511,611.

5 The aluminium plate subjected to anodic oxidation may be processed by dipping in an aqueous solution of alkali metal silicate, for example, sodium silicate, as described in U.S. Patents 2,714,066 and 3,181,461 or may be provided with an undercoating layer composed
10 of hydrophilic cellulose (e.g., carboxymethyl cellulose) containing water-soluble metal salts (e.g. zinc acetate) as described in U.S. Patent 3,860,426.

On the supports for the lithographic printing plates of the present invention, a known photosensitive
15 layer may be formed to produce photosensitive lithographic printing (pre-sensitized plates). These lithographic printing plates have excellent properties.

Compositions for the above-described photosensitive layers are described in our Specification No.
20 2 047 274A.

In the following Example, percentages are by weight.

EXAMPLE

After an aluminium sheet of purity 99.5% was
25 subjected to graining by a revolving nylon brush in an aqueous dispersion of pumice, it was etched using a 20% aqueous solution of sodium hydroxide so as to dissolve 8 g/m² aluminium. After adequately washing

the plate with water, it was washed with a 25% aqueous solution of nitric acid and then again with water to prepare a support.

The resulting plate was electrolyzed in an aqueous
5 nitric solution (7 g/l) at 22°C using an alternating wave form using the rectangular wave shown in Figure 4(b) under the condition shown in Table 1. It was then dipped in a 15% aqueous solution of sulfuric acid at 50°C for 3 minutes to clean the surface. Then, an
10 anodic oxide film of 3 g/m² was formed with using a 10% aqueous solution of sulfuric acid to produce Samples A, B, C, D, E and F.

On the resulting samples, the following photo-sensitive layer was provided at a coverage of 2.5 g/m²
15 (dried).

	Esterified compound of naphthoquinone-1,2-diazide-5-sulfonyl chloride and pyrogallol acetone resin (described in Example 1 in U.S. Patent 3,635,709)	0.75 g
20	Cresol Novolak Resin	2.00 g
	Oil Blue 603 (produced by Orient Chemical Co.	0.04 g
	Ethylene Dichloride	16 g
	2-Methoxyethylacetate	12 g

25 The resulting photosensitive lithographic printing plate was imagewise exposed to light for 60 seconds at a distance of 1 m using a 3 kw metal halide lamp, and it was then developed using an aqueous solution of sodium silicate having a molar ratio SiO₂/Na₂O of 1.2 and an
30 SiO₂ content of 1.5%. When printing was carried out in

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a conventional manner using the resulting lithographic printing plate, the results shown in Table 1 were obtained.

T A B L E 1

	(Sample A) 8 (g/m ²)	(Sample B) 8	(Sample C) 8	(Sample D) 8	(Sample E) 8	(Sample F) 18
Amount of etching						
Condition of electrolysis						
Anodic current density	35 (A/dm ²)	20	15	15	--	15
Anodic quantity of electricity	176 (coulomb/dm ²)	176	176	400	--	1,000
Qc/Qa	0.73	0.72	0.73	0.76	--	0.71
Va	23 (volts)	14	10	11	--	35
Vc	12 (volts)	8	6	7	--	17
Amount of anodic oxidation film	3 (g/m ²)	3	3	3	3	0.3
Cumulative frequency curve						
5%	2 (μ)	2.5	2	3	--	0.4
95%	5 (μ)	6.5	7	7	--	14
Density of secondary structure (third)	7 × 10 ⁷ (pit/cm ²)	3 × 10 ⁷	0.5 × 10 ⁷	17 × 10 ⁷	Absence	
Degree of pits uniformly dispersed in the secondary structure	Good	Good	Bad (non-uniform)	Bad (over-density)	Absence	Bad (over-density)
Mound	Presence	Presence	Presence	Absence	Presence	Absence
Printing durability	100,000 (sheets)	100,000	60,000	100,000	60,000	60,000
Contamination	Excellent	Excellent	Good	Bad	Excellent	Bad
Remarks	Invention	Invention	Comparison	Comparison	Comparison	Comparison

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CLAIMS



1. A support for a lithographic printing plate comprising an aluminium sheet, the surface of which has a grain structure as observed in enlargement of 2,000
- 5 times by a scanning electron microscope, comprising mounds, and pits each having a defined opening, which uniformly pierce the surface of said mounds, in a direction nearly perpendicular to the surface of the mound, and the pits are present in such a sparse uniform density that the face of the mounds is
- 10 ~~mounds~~ are still apparent.



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2. A support as claimed in Claim 1, in which the distribution of pit diameter is such that the pits corresponding to 5% and 95% on a cumulative frequency curve for pit diameter have a diameter of 3 μ or less, and 7 μ or less, respectively.
3. A support as claimed in Claim 2, in which the distribution of pit diameters is such that the pits corresponding to 5% and 95% on a cumulative frequency curve for pit diameter have a diameter of from 0.5 to 3 μ and 5 to 7 μ , respectively.
4. A support as claimed in Claim 1, 2 or 3, in which said pits are present in a density of 10^6 to 10^8 pits/cm².
5. A support as claimed in any one of Claims 1 to 4, additionally comprising an anodic oxide layer formed on said surface.
6. A support as claimed in Claim 1 and substantially as herein described.
7. A support for a lithographic printing plate, substantially as herein described with reference to Figs. 3(a) and 3(b) of the accompanying drawings or to Samples A and B in the foregoing Example.
8. A presensitized printing plate comprising a support as claimed in any one of Claims 1 to 7 and a photosensitive layer formed on said surface thereof.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office