



11 Publication number:

0 652 298 A1

(2) EUROPEAN PATENT APPLICATION

(21) Application number: **94117623.2**

2 Date of filing: 08.11.94

(5) Int. Cl.⁶: **C22F** 1/04, C22C 21/00, B41N 1/08, B22D 11/06

Priority: 09.11.93 JP 302244/93 15.11.93 JP 307108/93

Date of publication of application: 10.05.95 Bulletin 95/19

Designated Contracting States: **DE GB NL**

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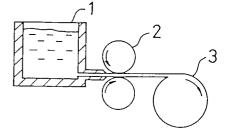
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Aluminum alloy support for planographic printing plate.

⑤ Disclosed is (i) an aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the plate, wherein a tensile strength of the aluminum alloy support is 15 kg/mm² or more and an offset stress of the aluminum alloy support is 10 kg/mm² or more when a heat treatment is conducted at 300 °C for 7 minutes and (ii) an aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the tabular plate to prepare an aluminum alloy support, and then graining the aluminum alloy support, wherein an average particle size of the intermetallic compounds in the aluminum alloy support is 0.5 to 8 μm, the number of intermetallic compounds is 500 to 10,000 per mm², and the number of the intermetallic compounds having the average particle size of 20 μm or more is 2% or less.

FIG. 1(A)



FIELD OF THE INVENTION

The present invention relates to an aluminum alloy support for planographic printing plate and more particularly relates to an aluminum alloy support which is superior in an electrolytically graining property. Furthermore, the present invention relates to an aluminum alloy support for planographic printing plate which does not soften easily even when a burning treatment is conducted after development of a coated photosensitive layer.

BACKGROUND OF THE INVENTION

As an aluminum alloy support for printing plate, particularly for offset printing plate, there is used an aluminum plate (including aluminum alloy plate).

In general, an aluminum plate to be used as a support for offset printing plate needs to have a proper adhesion to a photographic light-sensitive material and a proper water retention. For these purposes, the aluminum alloy support is subjected to a surface treatment such as a graining process and an anodizing process.

The graining process is conducted to make the surface of the aluminum alloy plate uniform and finely grained. This graining process largely affects a printing performance and a durability of the printing plate upon the printing process following manufacture of the plate. Thus, it is important for the manufacture of the plate whether such graining is satisfactory or not.

In general, an alternating current electrolytic graining method is used as a method of graining an aluminum support for a printing plate. There are a variety of suitable alternating currents, for example, a normal alternating waveform such as a sinewaveform, a special alternating waveform such as a squarewaveform, and the like. When the aluminum support is grained by alternating current supplied between the aluminum plate and an opposite electrode such as a graphite electrode, this graining is usually conducted only one time, as the result of which, the depth of pits formed by the graining is small over the whole surface thereof. Then, the durability of the grained printing plate during printing results in insufficient. Therefore, in order to obtain a uniformly and closely grained aluminum plate satisfying the requirement of a printing plate with deep pits as compared with their diameters, a variety of methods have been proposed as follows.

One method is a graining method to use a current of particular waveform for an electrolytic power source (JP-A-53-67507). (The term "JP-A" as used herein means an "unexamined published Japanese patent application".) Another method is to control a ratio between an electricity quantity of a positive period and that of a negative period at the time of alternating electrolytic graining (JP-A-54-65607). Still another method is to control the waveform supplied from an electrolytic power source (JP-A-55-25381). Finally, another method is directed to a combination of current density (JP-A-56-29699).

Further, known is a graining method using a combination of an AC electrolytic graining method with a mechanical graining method (JP-A-55-142695).

The grained aluminum alloy plate is subjected to an anodising treatment. Cases are sometimes met in which a hydrophilic treatment further is conducted. A photosensitive substance is coated thereon and dried to form a presensitized (PS) plate. Then, a printing treatment such as image printing, development and gumming is conducted on the PS plate. At this time, cases are sometimes met in which a burning treatment is conducted with soaking at about 200 to 300 °C for about 3 to 10 minutes after development, for improving the printing durability of the printing plate.

The burning treatment is effective to thermoset the remaining photosensitive resin on the aluminum plate. At the same time, however, it is liable to cause the heat softening of the aluminum plate. Usually, the burning treatment is conducted at a temperature range of about 200 to 280 °C for about 3 to 7 minutes, though it varies depending on image-forming compositions.

As the method of producing an aluminum support, on the other hand, known is a method in which an aluminum ingot is melted and held, and then cast into a slab (having a thickness in a range from 400 to 600 mm, a width in a range from 1,000 to 2,000 mm, and a length in a range from 2,000 to 6,000 mm). Then, the cast slab thus obtained is subjected to a scalping step in which the slab surface is scalped by 3 to 10 mm with a scalping machine so as to remove an impurity structure portion on the surface. Next, the slab is subjected to a soaking treatment step in which the slab is kept in a soaking furnace at a temperature in a range from 480 to 540 °C for a time in a range from 6 to 12 hours, thereby to remove any stress inside the slab and make the structure of the slab uniform. Then, the thus treated slab is hot rolled at a temperature in a range from 480 to 540 °C to a thickness in a range from 5 to 40 mm. Thereafter, the hot rolled slab is cold rolled at room temperature into a plate of a predetermined thickness. Then, in order to make the

structure uniform and improve the flatness of the plate, the thus cold rolled plate is annealed to thereby make the rolled structure, etc. uniform, and the plate is then subjected to correction by cold rolling to a predetermined thickness. Such an aluminum plate obtained in the manner described above has been used as a support for a planographic printing plate.

However, electrolytic graining is apt to be influenced by an aluminum support to be treated. If an aluminum support is prepared through melting and holding, casting, scalping, and soaking, even though passing through repetition of heating and cooling followed by scalping of a surface layer, scattering of the metal alloy components is generated in the surface layer, causing a drop in the yield of a planographic printing plate.

Furthermore, if an aluminum plate is prepared through the step of melting and holding, casting, scalping and soaking, the use of an alloy component made of nearly pure aluminum such as AA1050 is not tolerable for at a high temperature burning treatment, since the heat softening properties thereof are great.

In this connection, JP-A-61-51395 proposes adding 0.02 to 0.20% of zirconium, JP-A-61-272357 and JP-A-60-5861 propose specifying the intermediate annealing temperature, JP-A-59-67349 proposes specifying the conductivity.

In order to solve deterioration of the electrolytic graining property caused by the scattering of the alloy components, U.S. Patent No. 5,078,805 (corresponding to JP-A-3-79798) proposes a method of producing a support for planographic printing plate, which comprises continuously performing casting and hot rolling from molten aluminum to form a hot rolled coil of a thin plate, transforming the hot rolled coil into an aluminum support through cold rolling, heat treatment and correction, and finally, graining the aluminum support, as a method of reducing the scattering of aluminum support materials and thus improving the efficiency of electrolytic graining.

However, even the method proposed by U.S. Patent No. 5,078,805 still gives the non-uniformity of the heat softening property after the burning treatment. In addition, it is demanded to conduct the burning treatment at a higher temperature for a shorter period of time to improve the printing durability and to shorten the operating time.

SUMMARY OF THE INVENTION

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An object of the present invention is to provide an aluminum alloy support for planographic printing plate which is superior in graining property, thereby improving the yield of electrolytic graining as well as enabling the production of a planographic printing plate having low heat softening properties after a burning treatment.

The present inventors have made extensive studies on the relationship between aluminum support and electrolytic graining. As a result, the present inventors worked out the present invention.

In particular, the foregoing object of the present invention is accomplished with the followings:

- (i) an aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the plate, wherein an tensile strength of the aluminum alloy support is 15 kg/mm² or more and an offset stress of the aluminum alloy support is 10 kg/mm² or more when a heat treatment is conducted at 300 °C for 7 minutes.
- (ii) an aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the tabular plate to prepare an aluminum alloy support, and then graining the aluminum alloy support, wherein an average particle size of the intermetallic compounds in the aluminum alloy support is 0.5 to 8 μ m, the number of the intermetallic compounds is 500 to 10,000 per mm², and the number of the intermetallic compounds having the average particle size of 20 μ m or more is 2% or less.
- (iii) an aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, intermediate annealing, final cold rolling, and correction of the plate, wherein an tensile strength of the aluminum alloy support is 15 kg/mm² or more and an offset stress of the aluminum alloy support is 10 kg/mm² or more when a heat treatment is conducted at 300 °C for 7 minutes.

In a preferred embodiment, the molten alloy contains 0.05 wt% < Fe < 0.8 wt%, 0.01 wt% < Si < 0.3 wt%, 0.005 wt% < Ti < 0.1 wt%, 0.005 wt% < Cu < 0.2 wt%, less than 0.3 wt% of the other alloy components, based on the total amount of the molten aluminum alloy, and a balance of aluminum.

BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1(A) illustrates the concept of an embodiment of the continuous casting process of the present invention, in which 1 indicates a melt holding furnace, 2 indicates a twin-roller continuous casting machine, and 3 indicates a coiler.

Fig. 1(B) illustrates the concept of another embodiment of the continuous cast rolling process of the present invention, in which 1 indicates a melt holding furnace, 4 indicates a cold rolling machine, 7 indicates a twin-belt continuous casting machine, and 8 indicates a hot rolling machine.

Fig. 1(C) illustrates the concept of an embodiment of the cold rolling process of the present invention, in which 4 indicates a cold rolling machine.

Fig. 1(D) illustrates the concept of an embodiment of the heating process of the present invention, in which 5 indicates a heating machine.

Fig. 1(E) illustrates the concept of an embodiment of the correction process of the present invention, in which 6 indicates a correction machine.

Fig. 2 illustrates the concept of an embodiment of the casting process of the present invention, in which 9 indicates a molten aluminum supplying nozzle, 10 indicates a water-cooled casting mold, 11 indicates a cast ingot, and 12 indicates a cast ingot receiving tray.

DETAILED DESCRIPTION OF THE INVENTION

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In the present invention, as a method for continuously cast rolling a tabular plate directly from molten aluminum alloy, there can be used a method employing a cooling belt such as Hazelett method or a method employing a cooling roller such as Hunter method and 3C method. Since the Hazelett method continuously casts a thick plate, a hot rolling is subsequently conducted to make the thickness reelable. On the other hand, since the Hunter method or the 3C method makes it possible to directly cast a plate having the thickness of 10 mm or lower, a hot rolling machine is not necessary. Moreover, JP-A-60-238001, JP-A-60-240360, etc. disclose a method for preparing a coil of thin sheet.

In the present invention, molten aluminum alloy is rapidly cooled by the continuous casting method to make the alloy components of a solid solution in the matrix of the molten aluminum alloy more than the solid solution limit and make the tensile strength more than a prescribed value after cold rolling, intermediate annealing and final rolling more than a specific value, to provide the offset stress of 10 kg/mm² or more after heating at 300 °C for 7 minutes, whereby an aluminum alloy support for planographic printing plate which is hard to soft is provided even though a high temperature burning treatment is conducted.

Referring to Figs. 1(A), 1(B), 1(C), 1(D) and 1(E), an embodiment of the method of producing an aluminum alloy support according to the present invention will be further described. As shown in Fig. 1(A), the reference number 1 is a melt holding furnace in which an aluminum ingot is melted and retained. The molten aluminum ingot is then fed to twin-roller continuous casting machine 2. In some detail, a hot rolled coil of a thin plate having a thickness of 4 to 12 mm is directly formed from molten aluminum, then wound on coiler 3. (Alternatively, a continuous casting method using a cooling belt and a hot rolling may be applied as shown in Fig. 1(B)).

As shown in Fig. 1(C), the coil wound on coiler 3 is cold rolled to a thin plate of 0.3 to 3.0 mm using cold rolling machine 4. Subsequently, as shown in Fig. 1(D), an intermediate annealing may be conducted using heating machine 5. As heating (annealing) machine 5, there are various types such as a batch type, a continuous annealing type, an induced heating type. The temperature is elevated at a rate of 1 ° C/sec or more and the preferred temperature is 300 ° C or more. Then, the resulting thin plate is rolled again to a thickness of 0.1 to 0.5 mm using a cold rolling machine. Next, as shown in Fig. 1(E), correction is conducted using correcting machine 6. The aluminum plate thus obtained is subjected to a graining treatment. The correction may be conducted together with a finishing rolling.

Further, referring to the preparation conditions, the temperature in melt holding furnace 1 needs to be kept at not lower than the melting point of aluminum. The temperature in the melt holding furnace varies properly depending on the components of aluminum alloy. In general, it is not lower than 800 °C.

In order to inhibit the production of oxides of molten aluminum alloy and remove alkaline metals which impair the quality of the aluminum plate, the molten aluminum alloy is subjected to a proper treatment such as inert gas purge and fluxing.

The molten aluminum thus treated is subsequently subjected to casting by twin-roller continuous casting machine 2. There are many casting methods. Industrially operated are a twin-roller type represented by Hunter method and 3C method and a twin-belt type represented by Hazelett method. The optimum casting temperature is in the vicinity of 700 °C, though depending on the casting methods and the alloy

components. In a case of using Hunter method or 3C method, the solidifying of molten aluminum alloy and the rolling thereof between twin-rollers can be conducted continuously.

Using these continuous casting methods, rapid cooling of molten aluminum alloy is possible to enrich the alloy components which solid-dissolved in the matrix.

At this time, heating treatment such as intermediate annealing is conducted using heating machine 5 to control the size of crystal grains, which may be conducted with cold rolling using cold rolling machine 4. Next, correction is conducted using correcting machine 6 to provide a predetermined flatness. Then, an aluminum alloy support thus formed is grained. The correction may be conducted with the final cold rolling.

As a method of analyzing the intermetallic compounds in the aluminum alloy, there include a qualitative analysis such as a scanning electron microscopic (SEM) analysis, an electron probe microanalysis (EPMA), an X-ray analysis and an optical microscopic analysis and a quantitative analysis such as a thermal phenol extraction separation. The thermal phenol extraction separation is a system which utilizes the nature of dissolving metallic aluminum in thermal phenol, to extract and separate an intermetallic compound.

According to these methods, the number of extracted intermetallic compounds and the average particle diameter thereof can be evaluated. As a method of determining the particle size distribution, Coulter counter, etc. is used. These determinations should be conducted carefully, since there are a large number of intermetallic compounds having a particle size of 1 μ m or smaller. In the thermal phenol extraction separation, since the intermetallic compounds in a residue is separated by filtration using a membrane filter, it is of importance to optimize the mesh size of the filter to control to as fine as about 0.1 μ m.

As the method for graining the support for planographic printing plate according to the present invention, there is used mechanical graining, chemical graining, electrochemical graining or combination thereof.

Examples of mechanical graining methods include ball graining, wire graining, brush graining, and liquid honing. As electrochemical graining method, there is normally used AC electrolytic etching method. As electric current, there is used a normal alternating current such as sinewaveform or a special alternating current such as squarewaveform, and the like. As a pretreatment for the electrochemical graining, etching may be conducted with caustic soda.

If electrochemical graining is conducted, it is preferably conducted with an alternating current in an aqueous solution mainly composed of hydrochloric acid or nitric acid. The electrochemical graining will be further described hereinafter.

First, the aluminum support is etched with an alkali. Preferred examples of alkaline agents include caustic soda, caustic potash, sodium metasilicate, sodium carbonate, sodium aluminate, sodium gluconate, etc. The concentration of the alkaline agent, the temperature of the alkaline agent and the etching time are preferably selected from 0.01 to 20%, 20 to 90 °C and 5 sec. to 5 min., respectively. The preferred etching rate is in the range of 0.1 to 5 g/m².

In particular, if the support contains a large amount of impurities, the etching rate is preferably in the range of 0.01 to 1 g/m² (JP-A-1-237197). Since alkaline-insoluble substances (smut) are left on the surface of the aluminum plate thus alkali-etched, the aluminum plate may be subsequently desmutted as necessary.

The pretreatment is effected as mentioned above. In the present invention, the aluminum plate is subsequently subjected to AC electrolytic etching in an electrolyte mainly composed of hydrochloric acid or nitric acid. The frequency of the AC electrolytic current is in the range of 0.1 to 100 Hz, preferably 0.1 to 1.0 Hz or 10 to 60 Hz.

The concentration of the etching solution is in the range of 3 to 150 g/ ℓ , preferably 5 to 50 g/ ℓ . The solubility of aluminum in the etching bath is preferably in the range of not more than 50 g/ ℓ , more preferably 2 to 20 g/ ℓ . The etching bath may contain additives as necessary. However, in mass production, it is difficult to control the concentration of such an etching bath.

The electric current density in the etching bath is preferably in the range of 5 to 100 A/dm², more preferably 10 to 80 A/dm². The waveform of electric current can be properly selected depending on the required quality and components of aluminum support used but may be preferably the special alternating waveform described in U.S. Patent No. 4,087,341 (corresponding to JP-B-56-19280) and JP-B-55-19191. (The term "JP-B" as used herein means an "examined Japanese patent publication"). The waveform of electric current and the liquid conditions are properly selected depending on required electricity as well as required quality and components of aluminum support used.

The aluminum plate which has been subjected to electrolytic graining is then subjected to dipping in an alkaline solution as a part of desmutting treatment to dissolve smutts away. As such an alkaline agent, there may be used caustic soda or the like. The desmutting treatment is preferably effected at a pH value of not lower than 10 and a temperature of 25 to 60 °C for a dipping time as extremely short as 1 to 10 seconds.

The aluminum plate thus etched is then dipped in a solution mainly composed of sulfuric acid. It is preferred that the sulfuric acid solution is in the concentration range of 50 to 400 g/ ℓ , which is much lower than the conventional value, and the temperature range of 25 to 65 °C. If the concentration of sulfuric acid is more than 400 g/ ℓ or the temperature of sulfuric acid is more than 65 °C, the processing bath is more liable to corrosion, and in an aluminum alloy comprising not less than 0.3% of manganese, the grains formed by the electrochemical graining is collapsed. Further, if the aluminum plate is etched by more than 0.2 g/m², the printing durability reduces. Thus, the etching rate is preferably controlled to not more than 0.2 g/m².

The aluminum plate preferably forms an anodized film thereon in an amount of 0.1 to 10 g/m², more preferably 0.3 to 5 g/m².

The anodizing conditions vary with the electrolyte used and thus are not specifically determined. In general, it is appropriate that the electrolyte concentration is in the range of 1 to 80% by weight, the electrolyte temperature is in the range of 5 to $70\,^{\circ}$ C, the electric current density is in the range of 0.5 to $60\,^{\circ}$ A/dm², the voltage is in the range of 1 to $100\,^{\circ}$ V, and the electrolysis time is in the range of 1 second to 5 minutes.

The grained aluminum plate having an anodized film thus obtained is stable and excellent in hydrophilicity itself and thus can directly form a photosensitive coat thereon. If necessary, the aluminum plate may be further subjected to a surface treatment.

For example, a silicate layer formed by the foregoing metasilicate of alkaline metal or an undercoating layer formed by a hydrophilic polymeric compound may be formed on the aluminum plate. The coating amount of the undercoating layer is preferably in the range of 5 to 150 mg/m².

A photosensitive coat is then formed on the aluminum plate thus treated, imagewise exposed to light, and then developed to make a printing plate, which is then mounted in a printing machine for printing.

The present invention will be further described in the following non-limiting examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

EXAMPLES 1 AND 2 AND COMPARATIVE EXAMPLE 1

Using a continuous casting twin-roller thin plate machine as shown in Fig. 1(A), an aluminum plate material having a width of 1,000 mm and a thickness of 6 mm was formed and cold rolled to a thickness of 3 mm (Example 1), 2 mm (Example 2) and 0.5 mm (Comparative Example 1). After annealing at 400 °C, each of these materials was cold rolled (inclusive of correction) to a thickness of 0.3 mm. Thus, testing samples for Examples 1 and 2 and Comparative Example 1 were prepared.

COMPARATIVE EXAMPLES 2 AND 3

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Using a DC casting machine as shown in Fig. 2, cast ingot 11 was formed from molten aluminum supplying nozzle 9 through water-cooled casting mold 10, then was received on cast ingot receiving tray 12. The resulting cast ingot was subjected to scalping, soaking and hot rolling to provide an aluminum plate having a thickness of 6 mm, and further cold rolled to a plate thickness of 3 mm (Comparative Example 2) and 2 mm (Comparative Example 3). After annealing at 400 °C, the resulting aluminum plate was cold rolled (inclusive of correction) to a thickness of 0.3 mm.

Thus, testing samples for Comparative Examples 2 and 3 were prepared.

Table 1 shows details of testing materials for Examples 1 and 2 and Comparative Examples 1, 2 and 3.

45 TABLE 1

Sample No.	Casting Method	Thickness at Intermediate Annealing
1 (Ex. 1)	Continuous Casting	3.0 mm
2 (Ex. 2)	Continuous Casting	2.0 mm
3 (C.Ex. 1)	Continuous Casting	0.5 mm
4 (C.Ex. 2)	DC Casting	3.0 mm
5 (C.Ex. 3)	DC Casting	2.0 mm

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Using these samples, the tensile strength was evaluated and the offset stress was evaluated after heating these samples in an electric furnace at 300 °C for 7 minutes while measuring the temperature of these samples using a thermocouple detector.

The results are shown in Table 2.

TABLE 2

Tensile Strength Sample No. Offset Stress (after heating at 300 °C for 7 min. (kg/mm²) (kg/mm²) 17 12 1 (Ex. 1) 2 (Ex. 2) 16 11 14 3 (C.Ex. 1) 9 7 4 (C.Ex. 2) 17 5 (C.Ex. 3) 16 6

All of these comparative samples had the offset stress of 9 kg/mm² or lower.

The aluminum plates thus prepared were used as supports for planographic printing plate. These supports were etched with a 15% aqueous solution of caustic soda at 50°C to have an etching rate of 5 g/m², washed with water, desmutted with a 150 g/l sulfuric acid at 50 °C for 10 seconds, and then washed with water.

These supports were then subjected to electrochemical graining with the alternating waveform current described in JP-B-55-19191 in a 16 g/l nitric acid. The electrolysis conditions were 14 V for anode voltage V_A, 12 V for cathode voltage V_C, and 350 coulomb/dm² for anodic electricity.

Thereafter, the supports thus grained were subjected to chemical etching in 5% aqueous sodium hydroxide solution to an extent such that the dissolving amount of the aluminum plate reached 0.5 g/m², and desmutted with 300 g/l of a sulfuric acid solution at 60 °C for 20 seconds.

Further, the resulting supports were anodized with a direct current of 22 voltage, in which the distance between the electrodes was 150 mm, for 60 seconds in an aqueous solution of 150 g/l sulfuric acid having aluminum ion concentration of 2.5 g/l.

These supports were coated with a photosensitive layer having the following composition to have a coating amount of 2.0 g/m² after drying.

Photosensitive Layer Composition:

N-(4-hydroxyphenyl)-methacrylamide/2-hydroxyethyl	5.0 g
methacrylate/acrylonitrile/methylmethacrylate/methacrylic acid (= 15/10/30/38/7 in	
a molar ratio) copolymer (average molecular weight 60,000)	
Hexafluorophosphate salt of a condensate of 4-diazophenylamine and	0.5 g
formaldehyde	
Phosphorous acid	0.05 g
Victoria Pure Blue BOH (made by HODOGAYA CHEMICAL CO., LTD.)	0.1 g
2-Methoxyethanol	100.0 g

Each of the photosensitive planographic printing plates thus prepared was exposed to a metal halide lamp of 3 kw at a distance of 1 m for 50 seconds through a transparent negative film in a vacuum printing frame, developed with a developing solution of the following composition, subjected to burning treatment at 300°C for 7 minutes, and then gummed up with an aqueous solution of gum arabic to thereby prepare a planographic printing plate.

Developing Solution Composition:

Sodium sulfite	5.0 g
Benzyl alcohol	30.0 g
Sodium carbonate	5.0 g
Sodium isopropylnaphthalenesulfonate	12.0 g
Pure water	1,000 g

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By using the planographic printing plates thus prepared, printing test was preformed to evaluate the printability according to an usual procedure.

The results are shown in Table 3.

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TABLE 3

Sample No.	Printing Test Results			
1 (Ex. 1)	Good			
2 (Ex. 2)	Good			
3 (C.Ex. 1)	Poor			
4 (C.Ex. 2)	Poor			
5 (C.Ex. 3)	Poor			

From the results, it can be said that the planographic printing plates according to the present invention provide less heat softening against burning treatment, and excellent in the printing properties, as compared to conventional ones.

Furthermore, it is effective in cost saving for raw materials by simplification of the production step of an aluminum support, which greatly contributes to improve the quality and cost saving of a support for planographic printing plates.

EXAMPLES 3 TO 7 AND COMPARATIVE EXAMPLES 4 TO 8

Molten aluminum alloy was subjected to continuous cast rolling, cold rolling, heating and correction as shown in Fig. 1(A) to 1(E) to prepare ten kinds of aluminum plates having a final plate thickness of 0.4 mm, with varying the alloy components and the conditions of the intermetallic compounds as set forth in Table 4. Each of the aluminum plates was etched with a 15% aqueous caustic soda solution at $50\,^{\circ}$ C to have an etching amount of 7 g/m², desmutted with a 15 g/l nitric acid solution for 10 seconds, and then washed with water.

These supports were then subjected to electrochemical graining with the alternating waveform current described in JP-B-55-19191 in 15 g/l of aqueous nitric acid solution. The electrolysis conditions were 14 V for anode voltage V_A , 12 V for cathode voltage V_C , and 350 coulomb/dm² for anodic electricity. Thereafter, the supports thus grained were desmutted with 300 g/l of sulfuric acid at 60 °C for 20 seconds, then observed for grain shape using a scanning electron microscope.

To evaluate the amount of the intermetallic compounds of the plate, observation was conducted using EPMA mapping and an optical microscope to determine the number of the intermetallic compounds.

The number of the intermetallic compounds and the observation results by SEM are shown in Table 4.

TABLE 4

	% Alloy Components				Intermetallic Compounds			SEM Observation
	Fe	Si	Cu	Ti	Average size, (μm)	Numbers (/mm²)	Numbers of >20μ (%)	
Ex. 3:	0.2	0.05	0.01	0.01	1.5	4,000	0.5	0
Ex. 4:	0.4	0.08	0.02	0.02	1.8	8,000	0.6	0
Ex. 5:	0.6	0.15	0.02	0.02	2.0	1,200	0.4	0
Ex. 6:	1.0	0.20	0.01	0.01	6.0	1,000	1.8	ΟΔ
Ex. 7:	0.10	0.05	0.01	0.01	1.0	800	0.1	ΟΔ
Comp. Ex. 4:	0.2	0.05	0.01	0.01	9.0	700	10.0	ΔX
Comp. Ex. 5:	0.4	0.08	0.02	0.02	6.0	300	0.8	X
Comp. Ex. 6:	0.6	0.15	0.02	0.02	8.5	600	0.3	XX
Comp. Ex. 7:	0.00	0.00	0.00	0.00	0.4	800	0.01	X
Comp. Ex. 8:	0.8	0.5	0.03	0.03	0.8	15,000	1.80	ΔX
Notes: O: Good, ∆: Available, X: Unavailable								

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The results on Table 4 revealed that a sample according to Examples 3 to 7 which comprises the alloy components of 0.05% < Fe, 0.01% < Si < 0.3%, 0.005% < Cu < 0.2%, 0.005% < Ti < 0.1%, and the other alloy components of less than 0.3%, the average particle size of the metallic compounds of 0.5 to 0.5

As described above, the present invention can provide an aluminum alloy support for planographic printing plate, which is capable of providing further improved graining with good yield.

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

Claims

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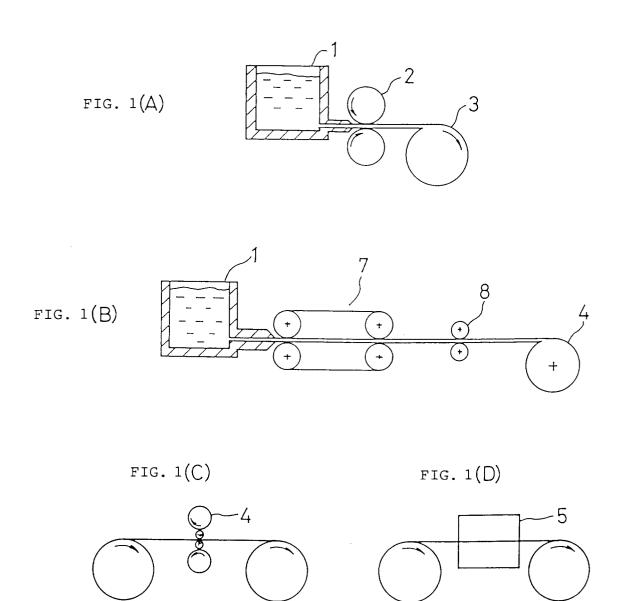
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- 1. An aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the plate, wherein a tensile strength of the aluminum alloy support is 15 kg/mm² or more and an offset stress of the aluminum alloy support is 10 kg/mm² or more when a heat treatment is conducted at 300 °C for 7 minutes.
 - 2. An aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, heating and correction of the tabular plate to prepare an aluminum alloy support, and then graining the aluminum alloy support, wherein an average particle size of the intermetallic compounds in the aluminum alloy support is 0.5 to 8 μm, the number of the intermetallic compounds is 500 to 10,000 per mm², and the number of the intermetallic compounds having the average particle size of 20 μm or more is 2% or less.
 - **3.** An aluminum alloy support for planographic printing plate prepared by a process which comprises subjecting molten aluminum alloy to continuous cast rolling to directly form a tabular plate, followed by cold rolling, intermediate annealing, final cold rolling, and correction of the plate, wherein a tensile strength of the aluminum alloy support is 15 kg/mm² or more and an offset stress of the aluminum alloy support is 10 kg/mm² or more when a heat treatment is conducted at 300 °C for 7 minutes.
- 4. An aluminum alloy support for planographic printing plate as claimed in Claims 1, 2 or 3, wherein the molten alloy contains 0.05 wt% < Fe < 0.8 wt%, 0.01 wt% < Si < 0.3 wt%, 0.005 wt% < Ti < 0.1 wt%, 0.005 wt% < Cu < 0.2 wt%, less than 0.3 wt% of other alloy components, based on the total amount of the molten aluminum alloy, and a balance of aluminum.



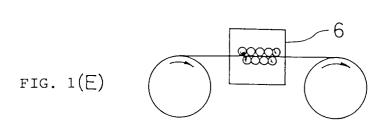
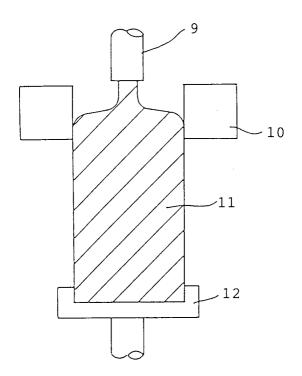


FIG. 2





EUROPEAN SEARCH REPORT

Application Number EP 94 11 7623

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Category	Citation of document with in of relevant pas		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Р,Х	EP-A-0 581 321 (FUJ) * page 5, line 29 - example 1 *		1-4	C22F1/04 C22C21/00 B41N1/08 B22D11/06
A	EP-A-0 289 844 (VERI AKTIENGESELLSCHAFT) * claims 1,8; table	EINIGTE ALUMINIUM-WERKE	1-4	B22D11700
D,A	EP-A-0 415 238 (FUJ) * example 1 *	I PHOTO FILM CO LTD)	1-3	
A	WO-A-91 07514 (ALCA LIMITED) * claim 1; figures		1,3	
D,A	PATENT ABSTRACTS OF vol. 8, no. 168 (C-& JP-A-59 067 349 (April 1984 * abstract *		1-3	
D,A	PATENT ABSTRACTS OF vol. 11, no. 136 (C & JP-A-61 272 357 (December 1986 * abstract *	-419) 30 April 1987	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22F C22C B41N B22D
A	W. HUFNAGEL 'ALUMIN 1983 , ALUMINIUM VE * page 1011 - page	RLAG , DUESSELDORF, DE	1-4	
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search	`- <u> </u>	Examiner
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CATEGORY OF CITED DOCUMENTS

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