(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 486 348 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.12.2004 Bulletin 2004/51

(51) Int Cl.[7]: **B41N 1/08**

(21) Application number: **04076742.8**

(22) Date of filing: **11.06.2004**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL HR LT LV MK

(30) Priority: **12.06.2003 EP 03076834**

(71) Applicant: **Fuji Photo Film B.V.**
5047 TK Tilburg (NL)

(72) Inventors:
- **Wiegers, Ronaldus J. T. H.**
  5237 NA 's-Hertogenbosch (NL)
- **Koopmans, Sipke Jan**
  5045 LP Tilburg (NL)
- **Sekiya, Toshiyuki**
  5045 JW Tilburg (NL)
- **Toda, Yuzo**
  5051 KZ Goirle (NL)

(74) Representative:
Winckels, Johannes Hubertus F. et al
Vereenigde
Nieuwe Parklaan 97
2587 BN Den Haag (NL)

(54) Aluminium alloy substrate for lithographic printing plate and method for producing the same

(57) Disclosed is a planographic printing plate with high quality and low cost obtained by casting molten aluminium directly and continuously into a thin aluminium plate, wherein the surface which reveals less ripple marks upon etching with an alkaline solution, is used for the manufacturing of the printing plate.

Disclosed furthermore is a planographic printing plate obtained by casting molten aluminium directly and continuously into a thin aluminium plate, wherein the side that is the top side during the casting process is used for the manufacturing of the printing plate.

EP 1 486 348 A2

Description

Field of invention

[0001] The present invention relates to a planographic printing plate and more particularly relates to a planographic printing plate in which the support is made using continuous casting.

Background of the invention

[0002] Conventional aluminium alloy substrates for a support for a lithographic printing plate are generally provided in the form of a 0.1 to 0.5 mm thick cold-rolled sheet made of an aluminium alloy such as JIS A1050, A1100, A3003, or the like. Such aluminium alloy cold-rolled sheets are generally produced by machining the surface of a semi continuous-cast (DC) slab or billet, homogenization heat-treating the billet when necessary, heating the billet to a selected temperature, hot-rolling the heated billet to a hot-rolled strip, cold-rolling the hot-rolled strip with an intermediate annealing between the cold rolling passes when necessary, and final cold rolling the strip to a cold-rolled sheet.

[0003] The aforementioned conventional process using a DC slab or billet has drawbacks in that the process steps are complicated and take much time, the production cost is high, the casting speed is slow, the rolling and heat treatment conditions are strict, and heat treatments must be carried out many times, and the process cannot provide an aluminium alloy support with stable properties.

[0004] Japanese Unexamined Patent Publication (Kokai) Nos. 3-79798 and 5-156414 disclosed a process of producing an aluminium alloy support for a lithographic printing plate, in which an aluminium alloy melt is continuously cast and rolled to form a strip, which is subjected to cold rolling, heat treatment, and straightening.

[0005] The process disclosed in Japanese Unexamined Patent Publication (Kokai) Nos. 3-79798 and 5-156414 also has drawbacks in that, although a continuous casting and rolling process is used, the support does not provide a sufficiently uniform surface when electrolytically grained and fails to have a satisfactory press life and that heat treatments are not conducted under suitable conditions.

[0006] The process described in European Patent No. 640694B1, in which an aluminium alloy printing plate support is manufactured with the continuous casting method which obtains improved electrolytic graining quality by tight specifications of alloying elements as Cu, Si and Fe is improving the situation, although it still does not provide a sufficiently uniform surface. More specifically a significant amount of surface defects are visible after the printing plate manufacturing which are named ripple marks. These ripple marks can only be noticed after the process of manufacturing the presensitised printing plate is completed. This can give a lot of waste and a very cost inefficient process.

Summary of the invention

[0007] It is an object of the present invention to provide a printing plate comprising at least a roughened and anodized aluminium plate provided with a heat or photosensitive material, wherein the roughened and anodized aluminium plate is formed from a thin aluminium support, which is made by casting molten aluminium directly and continuously, having a first suface and an opposite second surface where of the first and second surface the surface of the support which shows the least ripple marks upon etching with an alkaline solution has been used for roughening, anodizing and applying the heat or photo sensitive material.

[0008] The invention furthermore relates to a planographic printing plate by casting molten aluminium directly and continuously into a thin aluminium plate, wherein the side that is the top side during the casting process is used for the manufacturing of the printing plate.

[0009] In this respect directly and continuously casting has to be understood as at least encompassing various methods in which aluminium or aluminium alloy or similar suitable material is molten and then transferred to suitable equipment for forming thin sheet-like material in a continuous process. In this application aluminium has to be understood as including aluminium alloys.

[0010] The invention further relates to a method for producing said printing plates..

[0011] The invention also relates to the use of said planographic printing plates, in a printing process..

Brief Description of the drawing

[0012]

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; and

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

Detailed description

[0013] It is an object of the present invention to provide a printing plate comprising at least a roughened and anodized aluminium plate provided with a heat or photosensitive material, wherein the roughened and anodized aluminium plate is formed from a thin aluminium support, which is made by casting molten aluminium directly and continuously, having a first suface and an opposite second surface where of the first and second surface the surface of the support which shows the least ripple marks upon etching with an alkaline solution has been used for roughening, anodizing and applying the heat or photo sensitive material.

[0014] In this description the following definitions are used:

(aluminium) Support or (aluminium) strips: the product of a continuous casting process.

(aluminium) Plate: the support roughened by surface treatment.

[0015] Heat/photo sensitive printing plate: an aluminium plate provided with a heat and/or a photo-sensitive layer.

[0016] Planographic printing plate: an exposed(heat/photo) printing plate ready for usage in a printing process.

[0017] As a method for continuously cast rolling a tabular plate directly from molten aluminium 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. Among those a twin roller continuous casting method such as the Hunter method is preferable. Preferably a substantially horizontal casting method is used.

[0018] In this description basically or substantially has to be understood as at least including an angle with a horizontal plane of less than 30°, whereas an even smaller angle is preferred.

[0019] In the present invention, the molten aluminium alloy is rapidly cooled by the continuous casting. Referring to Figs. 1(A), 1(B), 1(C), 1(D) and 1(E), an embodiment of the method of producing an aluminium 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 aluminium ingot is melted and retained. The molten aluminium is then fed to a twin-roller continuous casting machine 2, 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).

[0020] 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 when necessary. 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 0.5 °C/sec or more and the preferred temperature is 300 °C or more. More preferably annealing can be applied at 480°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 correction may be conducted together with a finishing rolling.

[0021] The aluminium support thus obtained is subjected to a graining treatment. When an aluminium alloy support for a printing plate is electrolytically grained, it is a common practice to carry out as a pre-treatment chemical etching with an acid or alkali for degreasing or removal of oxide films from the surface of the substrate. The electrolytic graining process, as such, is an electrolytic etching process wherein an alternating current is applied where as a counter electrode graphite or the like is used to cause electrolytic etching, thereby forming pits on the surface of the substrate to provide a grained surface.

[0022] The above graining enhances the adhesion of a photosensitive film and improves the water retention, beneficial to printing performance, to the printing plate. Since adhesion and water retention should be provided uniformly over the whole surface of the printing plate, pits should be formed uniformly over the whole printing plate. For a printing plate provided with a photosensitive film, the grained surface should have a uniform appearance when viewed with the naked eye because the results of development after the exposure and development are evaluated by visual inspection.

[0023] Under nonuniform electrolytic graining is to be understood, that proper surface roughness cannot be attained due to excessive etching (dissolution type) or the presence of a region remaining unetched in the electrolytic etching. In this case, a problem occurs associated with the suitability of the plate for use in printing. Specifically, the adhesion of a photosensitive film to the aluminium plate becomes poor, and, further, the water retention or corrosion resistance in nonimage areas deteriorates, which in turn leads to tinting or scumming in nonimage areas during printing.

[0024] Nonuniform appearance of the grained surface means nonuniform color tone such as observation of streaks (a streak pattern) along the rolling direction or partial loss of gloss to give a cloudy appearance. This is caused by nonuniform chemical etching as a pre-treatment, leaving at least one region unetched or excessive etching, and electrolytic etching as an electrolytic graining treatment and a nonuniform metallic structure.

[0025] Without being bound to theory it is believed that the nonuniform metallic structure is attributable to nonuniform aluminium crystals orientation and aluminium crystal size, coarsening and nonuniform dispersion of an intermetallic compound, and the like. Even when the nonuniformity of the metallic structure is of an extent that is not detrimental to the uniformity of electrolytic graining (including pre-treatment) necessary for printing, it often makes the appearance of the grained surface remarkably nonuniform.

[0026] A nonuniform appearance, i.e., the presence of cloudy color shading, in the grained surface is very inconvenient to inspection of image areas after development. Specifically, the cloudy portions are present as they are in nonimage portions after development, and since they have a color tone similar to the image areas, it becomes difficult to visually judge whether or not the image areas can be satisfactorily developed.

[0027] One of the defects which negatively influences the quality of the final printing plate is the ripple mark defect; a wave like pattern. In the prior art methods the ripple marks become visible after a sequence of surface treatments and can only clearly be observed when the final product is almost completed. However the present inventors discovered that the marks can be made visible by simply etching the surface of the support by alkaline. Aqueous solutions of sodium or potassium hydroxide are the most preferable alkali solutions and the concentration is between 5 to 40 %. Etching operation can be done by simply dipping a sample in an alkali bath. Temperature is between 15 to 35 °C, dipping time is between 1 to 10 minutes, depending on alloy, thickness, casting conditions, etc.. By the alkali etching method, the more suitable surface for planographic printing plate can be determined. This method is in principle independent from the continuous cast method used. It can be applied to the supports obtained via any of the above mentioned continuous cast methods and even for such methods as described in for example US4523627 or WO9832559.

[0028] According to this invention, the side to be used for graining, hydrophilizing, coating, matting, etc. in order to form a good quality lithographic printing plate for supports manufactured via basically horizontal continuous casting methods, was found to be the side that is the top side during the casting process. The present inventors discovered that usage of the side that was the bottom side during the casting as surface for subsequent graining, hydrophilizing, coating, matting, etc. runs a risk of providing a non-uniform surface, in the form of ripple marks. Especially when casting operation extended over multiple coils over multiple lots, the top side during casting is much less prone to ripple mark formation, whereas the bottom side during casting quite often shows ripple marks. Usage of the top side drastically improves lot to lot fluctuation of casting in terms of ripple mark formation.

[0029] 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 aluminium. The temperature in the melt holding furnace varies depending on the components of aluminium alloy. In general, it is not lower than 800 °C.

[0030] In order to inhibit the production of oxides of molten aluminium alloy and remove alkaline metals which impair the quality of the aluminium plate, the molten aluminium alloy is subjected to a proper treatment such as inert gas purge and fluxing.

[0031] In the present invention, a preferable constitutional range of an alloy component is as follows. In order to obtain excellent properties for a support for a planographic printing plate, the preferable Fe content in the alloy is between 0.15 and 0.50 weight %, more preferably between 0.20 and 0.35 weight %. When Fe content is less than 0.15 weight %, mechanical strength of the sheet becomes insufficient. When Fe content is more than 0.50 weight %, electrical graining structure becomes uneven. The preferable Si content is between 0.05 and 0.20 weight %, more preferably between 0.10 and 0.15 weight %. When Si content is less than 0.05 weight %, response to electrical graining becomes weak. When Si content is more than 0.20 weight %, toning characteristic of the printing plate becomes worse. The preferable Cu content is between 0.005 and 0.040 weight %, more preferably between 0.008 and 0.025 weight %. When Cu content is less than 0.005 weight %, response to electrical graining becomes weak. When Cu content is more than 0.040 weight %, resulting electrical graining structure becomes too coarse leading the printing plate having worse toning characteristic. These values have been found to be valid for at least the alloys used in the experiments as discussed hereafter.

[0032] 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.

[0033] 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 sine waveform or a special alternating current such as square waveform, and the like. As a pre-treatment for the electrochemical graining, etching may be conducted with caustic soda.

[0034] 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.

[0035] First, the aluminium support is etched with 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 25%, 20 to 90 °C and 5 sec. to 5 min., respectively. The preferred etching rate is in the range of 0.1 to 15 g/m^2.

[0036] 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/m^2 (JP-A-1-237197). Since alkaline-insoluble substances (smut) are left on the surface of the aluminium plate thus alkali-etched, the aluminium plate may be subsequently desmutted as necessary.

[0037] The pre-treatment is effected as mentioned above. In the present invention, the aluminium 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.

[0038] The concentration of the etching solution is in the range of 3 to 150 g/l, preferably 5 to 50 g/l. The Content of aluminium 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.

[0039] The electric current density in the etching bath is preferably in the range of 5 to 100 A/dm^2, more preferably 10 to 80 A/dm^2. The waveform of electric current can be properly selected depending on the required quality and components of aluminium 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 aluminium support used.

[0040] The aluminium 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.

[0041] The aluminium plate thus etched is then dipped in a solution mainly composed of sulphuric acid. It is preferred that the sulphuric acid solution is in the concentration range of 50 to 400 g/l, and the temperature range of 20 to 70 °C. If the concentration of sulphuric acid is more than 400 g/l or the temperature of sulphuric acid is more than 70 °C, the processing bath is more liable to corrosion. Further, if the aluminium plate is etched by more than 0.4 g/m^2, the printing durability may be reduced. Thus, the etching rate is preferably controlled to not more than 0.4 g/m^2, more preferably not more than 0.2 g/m^2.

[0042] On the aluminium plate preferably an anodized film is formed in an amount of 0.1 to 10 g/m2, more preferably 0.3 to 5 g/m^2. 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 °C, the electric current density is in the range of 0.5 to 60 A/dm^2, the voltage is in the range of 1 to 100 V, and the electrolysis time is in the range of 1 second to 5 minutes.

[0043] The grained aluminium plate having an anodized film thus obtained is stable and excellent in hydrophilicity itself and thus can directly form a heat- or photosensitive coat thereon. If necessary, the aluminium plate may be further subjected to a surface treatment.

[0044] 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 aluminium plate.

[0045] Before applying the main coating layer, an undercoating layer may be applied. The coating amount of the undercoating layer is preferably in the range of 5 to 150 mg/m^2.

[0046] A heat- and/or photosensitive coating is then formed on the aluminium 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.

[0047] The present invention will be further described in the following nonlimiting examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

Examples

Example 1

[0048] By the continuous casting apparatus shown in Fig 1A, an aluminium strip (alloy AA1050) having a thickness of 5.0 mm was formed and coiled. The strip was cold rolled to a thickness of 2.2 mm, then annealed at 520°C for 8 hours, and further cold rolled to form an aluminium support of a thickness of 0.278 mm.

[0049] The aluminium support was subjected to alkali etching. The material was dipped in an aqueous solution of 25 weight % sodium hydroxide at 21°C for 7 minutes, rinsed by running water, and dried. The top surface at the casting did not reveal any ripple formation.

[0050] The top surface at the casting of the aluminium support was brush grained, etched with a 25% aqueous solution of sodium hydroxide at 50°C such that etched amount was 5 g/m2, after washing the etched plate with water, the plate was immersed in an aqueous sulphuric acid of 180 g/l at 50°C for 20 seconds to desmut the plate, and the plate was washed with water.

[0051] Furthermore the support was electrochemically grained in 9 g/l of an aqueous nitric acid solution using the alternating (wave form) electric current described in Japanese Patent No. JP-B-55-19191). As the electrolytic conditions, the anode and cathode voltages were selected to be V_A = 14V and V_o = 12V respectively so that the quantity of electricity in the anode time became 250 coulomb/dm2.

[0052] An anode surface oxide coating of 2.5 g/m2 was formed on the support in a 20% sulphuric acid, and then dried. Furthermore a silicate layer was formed on the surface by dipping in an 2.5 wt% aqueous sodium metasilicate solution at 25°C.

[0053] The thus obtained aluminium plate was examined for non-uniform parts: the plate appeared uniform in graining quality and appearance. No non-uniformity was observed.

[0054] The following composition was coated on the aluminium plate thus-prepared in a dry coated weight of 1.3 g/m2 to provide a photosensitive layer.

Photosensitive solution:	
Chemical	g/m2
Polyurethane consisting of 4,4'-diphenyltnethane diisocyanate / 1,6-hexamethylene diisocyanate / 2,2-bis(hydroxymethyl)-1-propionic acid / tetraethyleneglycol (80 / 20 / 20 / 80 mol %, MW = 150000)	1.01
Dodecylbenzene sulfonic acid salt of the condensate of p-diazodiphenylamine and paraformaldehyde	0.15
Phenylphosphonic acid	0.06
Victoria Pure blue	0.05
Surfactant	0.03
1-Methoxy-2-propanol	6
Methyl ethyl ketone	8
Methanol	5

[0055] The photosensitive planographic printing plate thus-prepared was subjected to exposure for 50 seconds with a metal halide lamp of 3 kW from a distance of 1 m. through a transparent negative film, and then it was subjected to development with a developing solution of the following composition, followed by gumming in gum arabic, whereby the planographic printing plates were prepared.

Developing solution:	
Chemical	g/l
Sodium sulphite	5.0
Benzyl alcohol	30
Sodium carbonate	5.0
Sodium isopropylnaphthalenesulfonate	12.0
Purified water	to make 1 lt

[0056] A printing test was carried out in a usual procedure using the planographic printing plate thus-prepared: 200.000 copies could be printed with a good quality.

Comparative example 1

[0057] By the continuous casting apparatus shown in Fig 1A, an aluminium strip (alloy AA1050) having a thickness of 5.0 mm was formed and coiled. The strip was cold rolled to a thickness of 2.2 mm, then annealed at 520°C for 8 hours, and further cold rolled to form an aluminium support with a thickness of 0.278 mm.
[0058] The aluminium support as such was subjected to alkali etching. The support was dipped in an aqueous solution of 25 weight % sodium hydroxide at 21°C for 7 minutes, rinsed by running water, and dried. The bottom surface at the casting revealed severe ripple formation.
[0059] This time, the side that was the bottom side during the casting process was submitted to the same steps as in Example 1. Upon examination, the plate shows an severe wave-like pattern, which renders the substrate unsuitable for further usage as a substrate for a lithographic printing plate.

Example 2

[0060] By the continuous casting apparatus shown in Fig 1A, an aluminium strip (alloy AA1050) having a thickness of 5.0 mm was formed and coiled. The strip was cold rolled to a thickness of 2.2 mm, then annealed at 380°C for 4 hours, and further cold rolled to form an aluminium support with a thickness of 0.278 mm. A similar test was repeated 10 times.
[0061] Each support formed as such was subjected to alkali etching as described in the Example 1. None of the top surfaces at the casting did reveal any ripple formation.
[0062] The top surface at the casting of the test material was brush grained, etched with a 25% aqueous solution of sodium hydroxide at 50°C such that etched amount was 5 g/m2, after washing the etched plate with water, the plate was immersed in an aqueous sulphuric acid of 180 g/l at 50°C for 20 seconds to desmut the plate, and the plate was washed with water.
[0063] Furthermore the support was electrochemically grained in 9 g/l of an aqueous nitric acid solution using the alternating (wave form) electric current in the manner as described in example 1. The quantity of electricity in the anode time became 180 coulomb/dm2.
[0064] An anode surface oxide coating of 3.5 g/m2 was formed on the support in a 20% sulphuric acid, and then dried.
[0065] Each aluminium plate thus obtained, was examined for non-uniform parts: all plates appeared uniform in graining quality and appearance. No non-uniformity was observed.
[0066] The following composition was coated on the aluminium plate thus-prepared in a dry coated weight of 1.7 g/m2 to provide a photosensitive layer.

Photosensitive solution:	
Chemical	g/m2
Ester compound of naphtoquinone-1,2-diazido-5-sulfonyl chloride and pyrogallol-acetone resin(*)	0.45
Cresol formaldehyde resin	1.10
t-Butyl phenol formaldehyde resin	0.05
Tetrahydrophtalic acid anhydride	0.09
Naphtoquinone-1,2-diazido-4-sulfonyl chloride	0.03
Ethyl violet	0.05
Megafac F-176 (fluorine containing surfactant, available from Dainippon Ink and Chemicals, Inc)	0.01
Methyl Ethyl ketone	6.0
1-Methoxy-2-propanol	4.0

(*) as disclosed in U.S. patent no. 3,635,709 (example 1)

[0067] The photosensitive planographic printing plate thus-prepared was subjected to exposure for 50 seconds with a metal halide lamp of 3 kW from a distance of 1m through a transparent positive film, and then it was subjected to development with a developing solution consisting of a 2 wt% aqueous solution of sodium silicate having a SiO_2/Na_2O ratio of about 1.1 and furthermore containing sodium ethylenediaminetetraacetate (0.01 g/l). The development process is followed by water rinsing and subsequent gumming in gum arabic, whereby the planographic printing plates were prepared.
[0068] A printing test was carried out in a usual procedure using the planographic printing plate thus-prepared.

200.000 copies with high quality were obtained from all 10 trials.

Comparative example 2

[0069] By the continuous casting apparatus shown in Fig 1A, an aluminium strip (alloy AA1050) having a thickness of 5.0 mm was formed and coiled. The strip was cold rolled to a thickness of 2.2 mm, then annealed at 380°C for 4 hours, and further cold rolled to form an aluminium support with a thickness of 0.278 mm. A similar test was repeated 10 times.

[0070] Each aluminium support formed as such was subjected to alkali etching as described in the Example 1. Five out of the ten bottom surfaces at the casting revealed strong ripple formation, and 5 revealed slight ripple formation.

[0071] The bottom surface at the casting of each trial was treated as described in Example 2, and examined for non-uniform parts: Five out of ten plates showed a wave-like pattern, which renders the support unsuitable for further usage as a support for a lithographic printing plate. Five plates showed slight wave-like pattern, which is acceptable but not desirable.

<u>Example 3</u>

[0072] By the continuous casting apparatus shown in Fig 1A, an aluminium strip (alloy AA1050) having a thickness of 5.0 mm was formed and coiled. The strip was cold rolled to a thickness of 2.2 mm, then annealed at 520°C for 8 hours, and further cold rolled to form an aluminium support with a thickness of 0.278 mm.

[0073] The aluminium support formed as such was subjected to alkali etching. The material was dipped in an aqueous solution of 25 weight % sodium hydroxide at 21°C for 7 minute, rinsed by running water, and dried. The top surface at the casting did not reveal any ripple formation. The bottom side during casting showed a clear, wave-like pattern know as ripple mark.

[0074] The upper surface at the casting of the support was etched with a 25% aqueous solution of sodium hydroxide at 50°C such that etched amount was 5 g/m2, after washing the etched plate with water, the plate was immersed in an aqueous sulphuric acid of 180 g/l at 50°C for 20 seconds to desmut the plate, and the plate was washed with water.

[0075] Furthermore the support was electrochemically grained in 10 g/l of an aqueous nitric acid solution using the alternating (wave form) electric current in the manner as described in example 1. The quantity of electricity in the anode time became 280 coulomb/dm2.

[0076] An anode surface oxide coating of 3.5 g/m2 was formed on the support in a 20% sulphuric acid, and then dried.

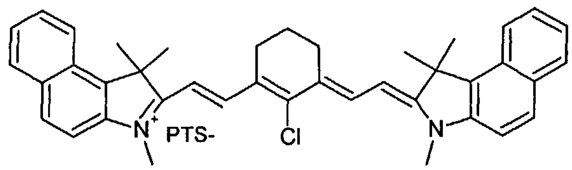
[0077] Each sample of thus obtained aluminium plate was examined for non-uniform parts: all plates appeared uniform in graining quality and appearance. No non-uniformity was observed.

[0078] The following composition was coated on the aluminium plate thus-prepared in a dry coated weight of 1.0 g/m2 to provide a heat-sensitive layer.

Chemical	g/m2
m,p-Cresol novolac (m/p ratio = 6/4; weight average molecular weight: 7,500; containing 0.8 wt.% of unreacted cresol)	0.95 g
Cyanine dye A (having the structure shown below)	0.025 g
Megafac F177 manufactured by DAINIPPON INK & CHEMICALS, INC.	0.01 g
Ethyl violet	
Methyl ethyl ketone	0.05
1-Methoxy-2-propanol	20.1 g
	2.7 g

Cyanine Dye A:

[0079]



[0080] The thus obtained heat sensitive plate was imaged in a Creo Trendsetter model 3244, and developed in the developer described in Example 2. Printing plates of excellent quality with good uniform appearance were obtained.

Claims

1. A printing plate comprising at least a roughened and anodized aluminium plate provided with a heat or photosensitive material, wherein the roughened and anodized aluminium plate is formed from a thin aluminium support, which is made by casting molten aluminium directly and continuously, having a first suface and an opposite second surface where of the first and second surface the surface of the support which shows the least ripple marks upon etching with an alkaline solution has been used for roughening, anodizing and applying the heat or photo sensitive material.

2. A printing plate comprising at least a roughened and anodized aluminium plate provided with a heat or photosensitive material, wherein the roughened and anodized aluminium plate is formed from a thin aluminium support, which is made by substantially horizontal casting molten aluminium directly and continuously, where a top surface of the support is used for roughening, anodizing and applying the heat or photo sensitive material.

3. A printing plate according to claim 1 or 2, wherein said casting has been done by a twin roller continuous casting method.

4. A printing plate as claimed in one of the claims 1 to 3, in which, after the aluminium has been continuously cast directly from molten aluminium into a thin aluminium strip, the aluminium strip has been subjected to cold rolling, optional heat treatment and flattening to obtain an aluminium support.

5. A printing plate according to claims 1 or 2, the surface roughening has been accompliced by graining at least at the side to be used for printing,.

6. A printing plate according to claim 1 or 2, in which anodizing layer, as expressed in weight per area, is from 0.1 to 10 g/m2

7. A printing plate according to any one of claims 1 -6, wherein an aluminium alloy has been used containing between 0.15 and 0.50 weight% FE and/or 0.05 and 0.20 weight% SI and/or 0.005 and 0.040 weight% CU.

8. A printing plate according to claim 8, wherein an aluminium alloy has been used containing between 0.20 and 0.35 weight% FE and/or 0.10 and 0.15 weight% SI and/or 0.008 and 0.025 weight% CU.

9. A printing accordingplate according claim 1, wherein an alkaline solution has been used for etching, preferably a sodium- or potassium hydroxide solution with a concentration between 5% to 40%.

10. A planographic printing plate made by heat- or photo exposing a plate according to claims 1 to 9 and optionally development of the plate to produce said planographic printing plate.

11. The use of the printing plate according to claim 10 in a printing process.

12. A method of producing a planographic printing plate by casting molten aluminium substantially horizontally directly

and continuously into a thin aluminium support, wherein the surface which reveals less ripple marks upon etching with an alkaline solution, is used for the manufacturing of the printing plate by applying a heat and/or photo sensitive material thereto.

13. A method according to claim 12, wherein said surface is the top surface during the casting.

14. A method according to claim 12 or 13, wherein said casting is done by a twin roller continuous casting method, whereby preferably after the aluminium is continuously cast directly from molten aluminium into a thin aluminium support it is subjected to cold rolling, optional heat treatment and flattening to obtain an aluminium support.

15. A method according to any one of claims 12 - 14, wherein the aluminium support, at least in the side to be used for printing, is subjected to surface roughening, in which preferably graining is used for said surface roughening.

16. A method according to any one of claims 12 - 15, wherein an aluminium alloy is used containing between 0.15 and 0.50 weight% FE and/or 0.05 and 0.20 weight% SI and/or 0.005 and 0.040 weight% CU, preferably an aluminium alloy containing between 0.20 and 0.35 weight% FE and/or 0.10 and 0.15 weight% SI and/or 0.008 and 0.025 weight% CU.

FIG. 1(A)

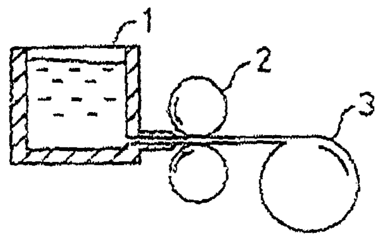


FIG. 1(B)

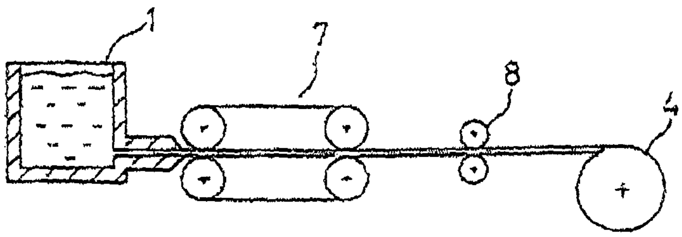


FIG. 1(C)

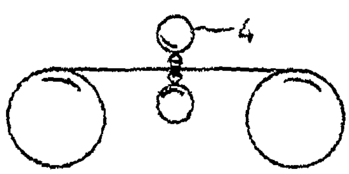


FIG. 1(D)

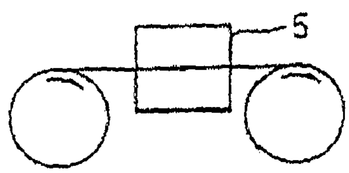


FIG. 1(E)