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(54) Aluminium alloy substrate for digitally imageable lithographic printing plate and process for producing the same

(57) Disclosed is a method for the production of an aluminium alloy support for a digitally imageable lithographic printing plate, comprising forming a support by carrying out the subsequent steps of:

- continuously casting a molten aluminium alloy to form a strip having a thickness less than 30 mm;
- cold rolling said strip to form said support;
- optionally a heat treatment step of said support;
- correction of the support; and
- mildly graining said support;

followed by providing a digitally imageable coating on said support, whereby said printing plate is obtained, characterized in that said aluminium alloy composition contains an iron amount between 0.15% by weight and 0.50% by weight; a silicon amount between 0.05% by weight and 0.20% by weight; and a copper amount between 0.005% by weight and 0.040% by weight.

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Description

Field of invention

[0001] The present invention relates to a method of producing a support for lithographic printing plates and more particularly relates to a method of producing an aluminium support which is superior for the production of digitally imageable lithographic printing plates (computer-to-plate imaging). The invention also relates to plates obtainable by that method.

Background of the invention

[0002] The development of lasers in recent years has been remarkable. In particular, high-output, compact solid-state lasers and semiconductor lasers having an emission area from near infrared to infrared have become readily available, as well as relatively low-priced lasers emitting visible light. These lasers are very useful as exposure light sources when making a plate directly from digital data from a computer or the like. This in contrast to the conventional method of plate making, in which the UV-sensitive layer on the lithographic printing plate precursor is exposed through a film by actinic light.

[0003] Various types of digitally imageable lithographic printing plates are known in the field. For example, EP-A-1 162 063 describes a positive acting IR-sensitive lithographic printing plate, based on a xylenol containing novolak. In this type of plates, distinction between the image and the non-image part of the printing plate is made based upon the increase in dissolution speed of the novolak containing coating layer in the developing liquid when this coating layer is exposed with infra-red radiation.

[0004] Another example is EP-A-0 672 954, which describes a negative working IR-sensitive lithographic printing plate. In this type of plate, the image is being formed through heat-induced insolubilisation of the coating layer. This type of plate usually requires a heating step between the IR-light exposure and the development step, in order to enhance the difference in dissolution speed between the image and the non-image area in the developer liquid.

[0005] Photopolymer plates generally contain a polymerizable monomer, a binder, a photoinitiator and a sensitising dye. For example, EP-A-0 985 683 describes a composition comprising a titanocene compound as a photoinitiator in a photopolymerizable composition that hardens upon exposure to light. By using specific dyes, the spectral sensitivity of the plate can be changed. A wide range of dyes for the wavelength range from 300 to 1200 nm is disclosed in EP-A-1 091 247.

[0006] The principle of the silver complex diffusion transfer process (hereinafter referred to as DTR process) is well known, see *e.g.* US-A-2 352 014 and "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde--The Focal Press--London and New York, (1972).

[0007] In the DTR process, the silver complex is imagewise transferred by diffusion from a silver halide emulsion layer to an image receptive layer and transformed therein into a silver image generally in the presence of physical development nuclei. For this purpose, the imagewise exposed silver halide emulsion layer is arranged so as to be in contact with or is brought into contact with the image receptive layer in the presence of a developing agent and a solvent for the silver halide, thereby to convert the unexposed silver halide into a soluble silver complex. In the exposed areas of the silver halide emulsion layer, the silver halide is developed into silver which is insoluble and, hence, cannot diffuse. In the unexposed areas of the silver halide emulsion layer, the silver halide is converted into a soluble silver complex and is transferred to an image receptive layer wherein the silver complex forms a silver image generally in the presence of physical development nuclei.

[0008] A specific example of the usage of the DTR method for digitally imageable lithographic printing plates is given in JP 2001-201858.

[0009] However, in all these types of digitally imageable lithographic printing plate material, the difference under various conditions of use between resistance to solubility of the unexposed portions (image portions) in a developer and solubility of the exposed portions (non-image portions) in a developer is still insufficient, which generally results in the problem that over-development or under-development occurs by variations in conditions of use.

[0010] One means of reducing problems with the above mentioned poor development latitude, is to lower the surface roughness of the roughened aluminium substrate. This may be done by omitting the usual mechanical graining process from the normal sequence of lithographic printing plate production or adjusting the settings of said process. In most cases this is sufficient to generate a plate which has sufficient development latitude to be practically usable.

[0011] However, the reduction of the surface roughness by omitting or changing the mechanical graining process has a considerable drawback: foreign material which is present on the aluminium substrate is not removed or not removed sufficiently by the mechanical graining. This will cause problems in the subsequent electrochemical graining process. Remaining metallic copper particles, for instance, will result in poor graining of (parts of the) aluminium surface, and defects like black streaks and shiny spots are the result of this.

[0012] Conventional aluminium alloy substrates as 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 Direct Chill (DC) slab or billet, homogenisation 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 optional intermediate annealing between the cold rolling passes when necessary, and final cold rolling the strip to a cold-rolled sheet.

[0013] An alternative method for the preparation of an aluminium support for lithographic printing plates is continuously supplying molten aluminium metal to cooled rollers or to a cooled belt, thus yielding a strip of aluminium. This method is also known as continuous casting (CC).

[0014] EP-A-0 415 238 and EP-A-0 615 801 describe the usage of this method for the manufacturing of conventionally imageable lithographic printing plates.

[0015] There remains a need for a digitally imageable lithographic printing plate without the problems described above combining a good developable latitude and a low amount of defects.

Summary of the invention

[0016] It is an object of the present invention to provide aluminium based lithographic printing plates that are digitally imageable so that they are suitable for computer to plate application, which plates have a good developable latitude and a low amount of defects. It has been found that such plates can be produced by a process comprising the step of continuous casting of molten aluminium. Thus in a first embodiment the present invention is directed to a process for producing a digitally imageable lithographic printing plate, comprising forming a support by carrying out the subsequent steps of: continuously casting molten aluminium to form a strip having a thickness less than 30 mm; cold rolling said strip to form a plate; optionally a heat treatment step of said plate; correction of the plate; and mildly graining said plate; followed by providing a digitally imageable coating on said support, whereby said printing plate is obtained.

[0017] It has been found that the continuous aluminium casting process provides for a support that is exceptionally suitable for providing plates for digitally imageable lithographic printing processes.

[0018] A further object of the invention is to provide a digitally imageable lithographic printing plate, comprising a support and a digitally imageable coating, which support may be prepared by the above-mentioned process of continuously casting molten aluminium to form a strip having a thickness less than 30 mm, followed by cold rolling, optional heat treatment, correction of the plate and then graining the aluminium support. In particular, the support for the plates of the present invention have an average surface roughness R_a of between 0.1 and 0.7 μm.

[0019] The present inventors have found that it is very important that the graining step is carried out carefully. The term "mildly graining" means that the mechanical graining step, if carried out is carried out such that the average surface roughness R_a of the resulting plates is less than 0.7 μm, preferably below 0.5 μm and more preferably below 0.4 μm.

[0020] In a preferred embodiment, any substantial mechanical surface graining is omitted in the preparation process of the supports for the plates of the present invention. It was found that in this way supports having a surface roughness that makes them very suitable for the applications of the present invention can be produced. In another embodiment of the present invention a digitally imageable lithographic offset plate is provided by a process comprising the steps of continuous casting molten aluminium so as to directly form a plate from the molten aluminium, cold-rolling and optionally heat-treating the plate to obtain an aluminium support, correction of the aluminium support, and surface-graining the aluminium support where the surface graining comprises an electrochemical graining process in dilute nitric acid, resulting in a support that has a centre line average surface roughness R_a of less than 0.4 micrometer or in dilute hydrochloric acid, resulting in a support that has a centre line average surface roughness R_a of less than 0.6 micrometer. The supports thus produced are also excellent for use as supports for plates according to the present invention. The supports prepared with the process in accordance with the present invention may be used to prepare printing plates. These plates are thus based on a support having a good developable latitude and a low amount of defects, which makes them structurally different from the plates known from the prior art.

Detailed description of the invention

[0021] A suitable method for continuously cast rolling a tabular plate directly from molten aluminium alloy, is a method employing a cooling belt, such as the Hazelett method or a method employing a cooling roller, such as the Hunter method and the 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. JP-A-60-238001, JP-A-60-240360, and other publications disclose a method for preparing a coil of thin sheet. A twin roller continuous casting method, such as the Hunter method, is preferred.

[0022] 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. In Fig. 1(A), the reference number 1 refers to 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 schematically in Fig. 1(B).

[0023] As shown schematically in Fig. 1(C), the coil wound on coiler 3 is cold rolled to a thin plate of 0.3 to 3.0 mm thickness using a cold rolling machine 4. Subsequently, as shown schematically 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 or 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. 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 schematically in Fig. 1(E), correction is conducted using correcting machine 6. The correction may be conducted together with a finishing rolling.

[0024] In the present invention, a suitable alloy composition is as follows. In order to obtain an excellent property for a support for a lithographic printing plate, the preferred Fe content in the alloy is between 0.15 and 0.50 weight%, more preferably between 0.22 and 0.26 weight%. When the Fe content is less than 0.15 weight%, mechanical strength of the sheet may become insufficient. When Fe content is more than 0.50 weight%, electrical graining structure may become uneven.

[0025] The preferred Si content is between 0.05 and 0.20 weight%, more preferably between 0.10 and 0.18 weight%. When the Si content is less than 0.05 weight%, response to electrical graining becomes weak. When the Si content is more than 0.20 weight%, toning characteristics of the printing plate may become unacceptable.

[0026] The preferred Cu content is between 0.005 and 0.040 weight%, more preferably between 0.005 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.

[0027] These values of Fe, Si and Cu have been found to be suitable as will be illustrated in the examples given hereafter.

[0028] For graining the support for lithographic printing plate according to the present invention, preferably no mechanical graining is used. It is important to obtain a low surface roughness in the case of digitally imageable lithographic printing plates, since this provides for a correspondingly good development latitude. Mechanical graining can be used when executed under mild conditions. Examples of mechanical graining methods include ball graining, wire graining, brush graining, and liquid honing. In order to obtain the required surface roughness, preferably electrochemical graining is used, preferably in the substantial absence of any mechanical graining.

[0029] 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, for example with caustic soda.

[0030] If electrochemical graining is conducted, it is preferably conducted with an alternating current in an aqueous solution comprising hydrochloric acid or nitric acid. The electrochemical graining will be further described hereinafter.

[0031] Prior to the electrolytical graining, the aluminium support is etched with an alkaline agent. Preferred 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.

[0032] In the present invention, the aluminium plate is preferably 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 suitably in the range of 0.1 to 100 Hz, preferably 0.1 to 1.0 Hz or 10 to 60 Hz.

[0033] The concentration of dissolved aluminium in the etching solution is suitably in the range of 3 to 150 g/dm^3, preferably 5 to 50 g/ dm^3. The solubility of aluminium in the etching bath is preferably in the range of not more than 50 g/ dm^3, more preferably 2 to 20 g/ dm^3. The etching bath may contain additives as necessary. However, in mass production, it is difficult to control the concentration of such an etching bath.

[0034] 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 the waveform is preferably the special alternating waveform described in US-A-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.

[0035] The aluminium plate which has been subjected to electrolytic graining is then preferably subjected to dipping

in an alkaline solution as a part of desmutting treatment to dissolve smuts 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.

[0036] The aluminium plate thus etched is then suitably 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, and the temperature range of 20 to 70 °C. If the concentration of sulfuric acid is more than 400 g/l or the temperature of sulfuric 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.

[0037] The aluminium plate preferably forms an anodised film thereon in an amount of 0.1 to 10 g/m^2, more preferably 0.3 to 5 g/m^2. The anodising 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.

[0038] The grained aluminium plate having an anodised film thus obtained is stable and excellent in hydrophilicity itself and thus can directly be provided with a heat- or photosensitive coating thereon. If necessary, the aluminium plate may be further subjected to a surface treatment.

[0039] For example, a silicate layer formed by the meta silicate of alkaline metal or an undercoating layer formed by a hydrophilic polymeric compound may be formed on the aluminium plate.

[0040] The surface roughness of the support obtained according to the present invention is of importance, since a too high surface roughness of the support will lead to a poor development latitude. The surface roughness is suitably measured according to JIS B060. The stylus radius for measurements of surface roughness R_a is typically 5 μm, and with this stylus, the following limits have been established. The centre line average surface roughness Ra of the thus obtained support has a value of 0.2 - 1.0 μm. For the usage in digitally imageable lithographic printing plates, the surface roughness is preferably 0.15 - 0.40 μm when nitric acid is used in the electrolytical graining process. In the case hydrochloric acid is used in the electrolytical graining process, the preferred centre line average surface roughness R_a lies between 0.40 and 0.65 μm.

[0041] 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.

[0042] A heat- and/or light sensitive coating is then formed on the aluminium plate thus treated. This heat or photosensitive coating can be positive or negative working. The heat- or light sensitive coating can be sensitive for electromagnetic radiation with a wavelength ranging between 380 and 1100 nm. Specific wavelengths of laser diodes or solid state lasers that can be used for the imagewise exposure of the lithographic printing of the present invention include 405 nm (violet laser), 488 nm (Ar-ion laser), 532 nm (FD-YAG laser), 633 (He-Ne laser), 670, 675, 680 nm (red laser diodes), 760, 780 nm (IR laser diodes), 830 nm (IR laser), 1064 nm (YAG-laser).

[0043] Examples of the photosensitive coating for digitally imageable lithographic offset plates for which the present invention is useful are: negative working photopolymerizable systems, comprising one or more photoinitiators and mono- and/or oligomers; negative working thermal printing plates; positive working thermal printing plates; printing plates based on the silver salt diffusion transfer process; and the like.

[0044] The thus obtained lithographic printing plate precursor may then be imagewise exposed to digitally controlled (laser) light.

[0045] After exposure, the plate can be subjected to a heat treatment if the nature of the printing plate requires so.

[0046] Next, the plate can be developed in a developing liquid. This liquid can be an aqueous alkaline solution, but also other solutions are known in the art. The resulting plate has almost no copper defects, while the development latitude is excellent.

[0047] The present invention will be further described in the following nonlimiting examples. Unless otherwise indicated, all amounts (parts, percentages, ratios, etc.) are by weight.

Examples

Example 1

[0048] Using the continuous casting apparatus shown schematically 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 a test material of a thickness of 0.278 mm.

[0049] The molten aluminium alloy had the following composition:

- Fe 0.23 wt%

- Si 0.10 wt%
- Cu 0.005 wt%
- Al 99.5 wt%

[0050] The thus produced aluminium strip was etched with a 25% aqueous solution of sodium hydroxide at 50 °C such that the etched amount was 5 g/m^2. After washing the etched strip with water, the strip was immersed in an aqueous sulphuric acid of 180 g/dm^3 at 50 °C during 20 seconds to desmut the strip, and the strip was washed with water.

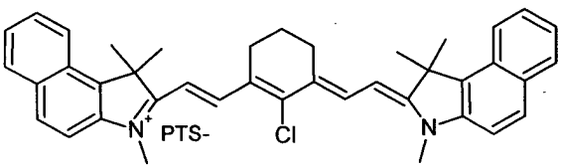
[0051] Furthermore the support was electrochemically grained in 9 g/dm^3 of an aqueous nitric acid solution using the alternating (wave form) electric current described in Japanese Patent No. JP-B-55-19191). As the electrolytic conditions, the anode and cathode voltages were selected to be V_A=14 V and V_o=12 V respectively, so that the quantity of electricity in the anode time became 250 coulomb/dm^2.

[0052] An anode surface oxide coating of 2.5 g/m^2 was formed on the support in a 20% sulfuric 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. After these steps, the centre line average surface roughness R_a was measured and found to be 0.32 µm.

[0053] The following composition was coated on the support thus-prepared in a dry coated weight of 1.3 g/m^2 to provide a positive working, thermal photosensitive layer. Thus, a lithographic offset plate, imageable with a digitally controlled 830 nm laser and having a good development latitude can be obtained.

Compound	g/m^2
m,p-Cresol novolac (m/p ratio = 6/4; weight average molecular weight: 7500; containing 0.8 wt.% of unreacted cresol)	0.95
Cyanine dye A (having the structure shown below)	0.025
Megafac F177 manufactured by DAINIPPON INK & CHEMICALS, INC.	0.01
Ethyl violet	0.05
Methyl ethyl ketone	20.1
1-Methoxy-2-propanol	2.7

Cyanine Dye A:



[0054] Under the above mentioned conditions, 5 coils of each 6000 m length were prepared. These coils were inspected for copper-related defects on the aluminium support; on these coils no copper related defects were found.

Example 2 (comparative)

[0055] In the same way as Example 1 a lithographic offset plate was made with the exception, that before the electrolytic graining a coarse mechanical graining step was included, carried out with a nylon brush (No. 8) and an aqueous suspension of 800 mesh pumice stone. This mechanical graining step resulted in an average surface roughness Ra of 0.75 µm. This was followed by thorough rinsing with water. The development latitude of the resulting offset plate was found to be insufficient.

Example 3 (comparative)

[0056] In the same way as described in Example 1 a substrate for lithographic offset plate was made with the following alloy composition: Al 99.2%, Fe 0.7 wt%, Si 0.2 wt%, Cu 0.010 wt%. The appearance of the grained substrate was streaky, and not sufficient for usage as substrate for a lithographic printing plate.

Example 4

[0057] A lithographic offset plate was made in the same way as described for Example 1 except, that hydrogen chloride was used as an electrolyte during electrochemical etching. A good development latitude and no copper defects were obtained.

Example 5 (comparative)

[0058] In the same way as for Example 2 a lithographic offset plate was manufactured but instead of a continuous cast coil a DC coil was used. DC cast aluminium coils were prepared from an aluminium ingot through a process including melting, holding, slab casting, scalping and soaking. The aluminium was hot-rolled, cold-rolled, annealed, corrected and grained to yield a strip that was chemically and dimensionally comparable to the continuously cast strip that is mentioned above. The development latitude was poor.

Example 6 (comparative)

[0059] A lithographic offset plate was manufactured in the same way as for Example 1 except, that a DC casted aluminium coil was used. The development latitude was good, but the defect level was too high.

[0060] The results of Examples 1 to 6 are shown in the table below.

Example	Alloying elements (Fe/Si/Cu) (wt%)	Casting method	Mechanical graining	Electrolytical graining liquid	Surface roughness R_a	Development latitude (10 = good; 0=insufficient)	Graining quality (10=good, 0=insufficient)	Cu-related defect level (defects/1000 m^2)
1	0.23/0.10/0.005	CC	No	HNO_3	0.32	9	8	0
2*)	0.23/0.10/0.005	CC	Yes	HNO_3	0.75	3	8	0
3*)	0.70/0.20/0.010	CC	No	HNO_3	0.33	9	4	1
4	0.23/0.10/0.005	CC	No	HCl	0.54	8	7	0
5*)	0.23/0.10/0.005	DC	Yes	HNO_3	0.49	3	9	1
6*)	0.23/0.10/0.005	DC	No	HNO_3	0.32	9	9	9

*): Comparative example

Example 7

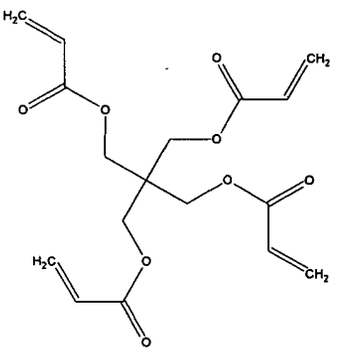
[0061] An aluminium coil (grade 1050AA) was prepared by twin-roll continuous casting of molten aluminium alloy (composition Al 99.5 wt%, Fe 0.26 wt%, Si 0.14 wt%, Cu 0.020 wt%) into a strip of 6 mm thickness. This strip was then cold rolled, annealed at 520 °C during 8 hours, again cold rolled and corrected to yield a coil of 0.30 mm thickness. The thus obtained coil was etched by immersing in a 10% aqueous solution of sodium hydroxide at 70 °C during 60 seconds, followed by successively washing with running water, a 20% nitric acid solution for neutralization, and water. The surface of the aluminium plate was then electrolytically roughened in a 1% aqueous solution of nitric acid by the application of an alternating current in the form of a sinusoidal wave at the applied voltage (Va) of 12.7 V. The electrical charge was set to 300 C/dm at the anode side. At this stage, the surface roughness of the aluminium plate was measured and found to be 0.29 μm in terms of Ra units. Subsequently, the aluminium plate was immersed in a 30% aqueous solution of sulfuric acid at 55 °C during 2 minutes to desmut the plate. The aluminium plate was then anodised in a 20% aqueous solution of sulfuric acid at 33 °C during 50 seconds at a current density of 5 A/dm^2, with the surface-grained surface of the aluminium plate serving as a cathode. The result was that the anodised layer with a thickness of 2.7 g/m^2 was deposited on the anode.

[0062] An undercoating of phenylphosphonic acid 0.2% b/w in methanol/water 16:1 was applied, so that the total amount of phosphorous (P) was about 0.05 g/m^2.

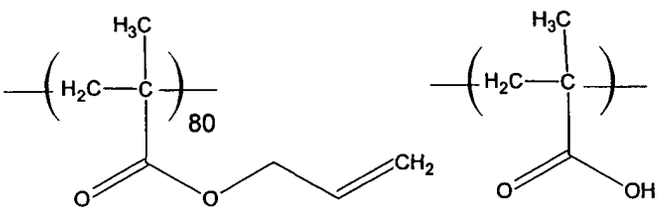
[0063] The following components were mixed to prepare a coating liquid for formation of the light-sensitive layer:

Compound	Parts by weight
Ethylenically-unsaturated bond containing compound B	1.7
Linear organic polymer C	1.9
Sensitizer D	0.15
Photopolymerization initiator E	0.30
Additive F	0.50
Fluorine-containing surfactant ("Megafac F-177" (trademark), made by Dainippon Ink & Chemicals, Incorporated)	0.03
Thermal polymerization inhibitor (N-nitrosohydroxylamine aluminium salt)	0.01
epsilon -type copper phthalocyanine dispersion	0.2
Methyl ethyl ketone	30.0
Propylene glycol monomethyl ether	30.0

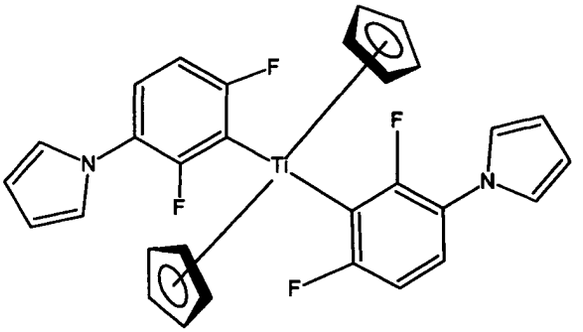
[0064] Ethylenically-unsaturated bond containing compound B:



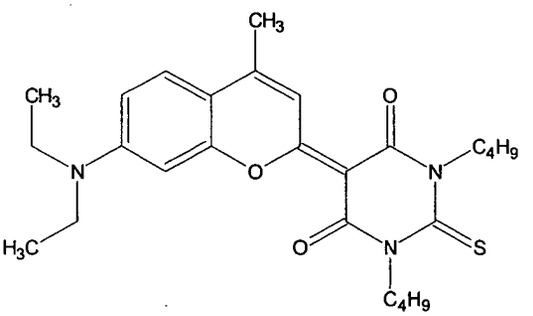
[0065] Linear organic polymer C:



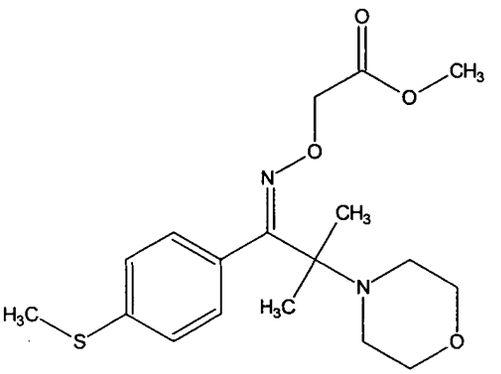
[0066] Sensitizer D:



[0067] Photopolymerization initiator E:



[0068] Additive F:



[0069] After drying at 100°C, the coating amount was measured to be 1.5 g/m^2.

[0070] Subsequently, a topcoating containing 3% aqueous solution of polyvinyl alcohol with a degree of saponification of 98 mol% and a degree of polymerisation of 500 was coated on the photosensitive layer so that the coating amount was 2.5 g/m^2 on a dry basis and dried at 120 °C.

[0071] The coil was automatically inspected with an automated laser inspection system. On this coil, no copper related defects were found. To demonstrate that the thus obtained plate is digitally imageable, it was exposed with a 532 nm FD-YAG laser ("PlateJet 4" (trademark), made by Cymbolic Sciences, Inc.) with an intensity of 100 mW. With an exposure of 100 μJ/cm^2 under the standard exposure conditions, a solid image and dot images (with an increased dot percent from 1 to 99% by 1%) were subjected to scanning using the above-mentioned light sources at a density of 4000 dpi and 175 rays/inch.

[0072] After completion of the light exposure, each PS plate was subjected to development under the standard conditions using a commercially available automatic processor ("LP-850P2" (trade name), made by Fuji Photo Film Co., Ltd.) containing LP-DS, a developer for photopolymerizable plates commercially available from Fuji Photo Film Co,

Ltd.. A good, solid image was obtained, and the non-image area was free from coating residues.

Example 8 (comparative)

[0073] Molten aluminium (AA1050, same alloy composition as Example 7) was cast according to the DC method into slabs of 450 mm x 1200 mm x 3500 mm. These slabs were subjected to 7 mm scalping per surface, soaking at 550 °C for 12 hours, and were then hot-rolled at 500 °C to produce a plate of 5 mm thickness. This plate was cold rolled, annealed at 520 °C for 8 hours, again cold rolled and corrected to yield a coil of aluminium of 0.30 mm thickness.

[0074] This coil was grained mechanically with a nylon brush (No. 8) and an aqueous suspension of 800 mesh pumice stone, followed by thorough rinsing with water.

[0075] Next, the coil was etched, grained and anodised in the fashion of Example 7, yielding a substrate with a centre line average surface roughness R_a of 0.60 μm.

[0076] The thus obtained support was coated with undercoating, photosensitive layer and topcoating as mentioned in Example 7.

[0077] Upon inspection, no copper related defects were observed on the coil.

[0078] Exposure and development were executed as mentioned in Example 7. Although the quality of the image area was good, the non-image area showed undeveloped parts where the mechanical graining had made deep cuts into the substrate.

Example 9 (comparative)

[0079] A coil was produced in the fashion of Example 7, this time without applying the mechanical graining. The centre line average surface roughness R_a after the completion of the anodising step was 0.31 μm. Exposure and development showed a good image area and a clean non-image area.

[0080] Inspection of the coil yielded 10 copper related defects per 1000 m^2.

Example 10

[0081] An aluminium coil (grade AA1050, alloy composition as in Example 1) was prepared by twin-roll casting of molten aluminium alloy into a strip of 3 mm thickness. This strip was then cold rolled, annealed at 380 °C for 4 hours, again cold rolled and corrected to yield a coil of 0.15 mm thickness.

[0082] On this material, an etching and graining process was carried out comprising the steps of treatment with 20% sodium hydroxide solution at 70 °C which removes 5 g/m^2 of the surface, treatment with 20% nitric acid, electrolytic graining in a 1% hydrochloric acid solution, using a 12.7 V sinusoidal alternating current with a total charge application of 160 Cb/dm^2, treatment with 30% sulfuric acid at 55 °C, and anodising in 20% sulfuric acid to yield an aluminium oxide layer of 2.7 g/m^2. Finally, the substrate was treated with a 5% 40 °C phosphoric acid solution during 30 seconds. The centre line average surface roughness R_a of the substrate was 0.45 μm.

[0083] A silver nuclei containing hydrosol was prepared in the following way:

Solution A:	
Trisodium Citrate (40%)	3.5 g
FeSO4 $7H_2O$ (30 wt%)	2.5 g

Solution B:	
$AgNO_3$ (10%)	2.5 g

[0084] The solutions A and B were mixed after adding solution B to A at a rate of 100 cc/min. The excess citrate, iron and sodium ions were removed by ultra-filtration, and an Ag-sol was obtained. This Ag sol was coated onto the substrate obtained above, yielding a image acceptance layer containing 2 mg/m^2 Ag.

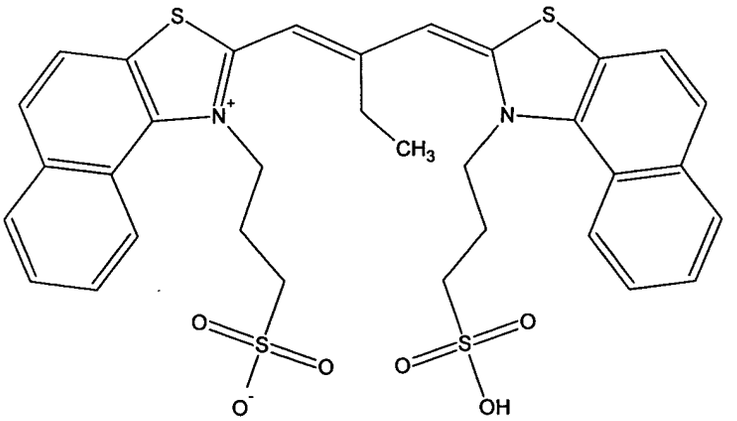
[0085] A silver-halide emulsion layer was prepared in the following way:

[0086] A silver nitrate solution containing 1.0 mol/dm^3 $AgNO_3$ and $3x10^{-7}$ mol/l rhodium ammonium chloride was prepared. A halide solution containing KBr (0.1 mol/l) and NaCl (0.9 mol/l) was prepared. The silver nitrate and the halide solutions were added to a solution containing 0.1 mol/l NaCl, $5x10^{-7}$ mol/l iridium hexachlorate, and $1x10^{-4}$ mol/l 1,3-dimethyl-2-imidazolinethione, at 45 °C during 30 minutes in a double jet process under continuous agitation. The size of the silver halide crystals was 0.28 μm, and the crystals contained 90 mol% of AgCl.

[0087] The crystals were flocculated according to a well-know method, and after rinsing gelatine was added. The emulsion was then adjusted to pH 6.5 and pAg 7.5. 5 mg sodium thiosulfate and 8 mg chloroauric acid were added per mol silver. The chemical sensitisation process was carried out for 60 minutes at 60 °C, using 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as a stabilizer.

[0088] Spectral sensitisation was carried out with $4x10^{-4}$ mol/mol Ag of dye G.

Dye G:



[0089] The thus obtained emulsion was coated onto the substrate carrying the Ag-nuclei, resulting in a silver content of 1.5 g/m^2 and a gelatine coated weight of 1.5 g/m^2.

[0090] Inspection of the coil made in the fashion described above yielded 1 copper related defect per 1000 m^2.

[0091] The thus obtained printing plate precursor of the diffusion transfer type (DTR) was exposed by a digitally controlled semiconductor laser with a wavelength of 670 nm, and developed at 21°C during 25 seconds in a developing solution of the following composition:

Developing solution for DTR plates	Amount
Sodium Hydroxide	16 g
Sodium Sulfate (anhydr)	140 g
Hydroquinone	27 g
1-phenyl-1-methyl-3-pyrazolidinone	3.5 g
Sodium Thiosulfate (anhydr)	13 g
2-methylaminoethanol	28 g
Glycerol	54 g
De-ionised water	1000 g

[0092] The pH of this solution was 13 at 24°C

[0093] Subsequently, in order to remove the silver halide emulsion layer developed fro the image forming material, the developed image forming material was rinsed with water for 30 seconds at 30°C. Next, the following finishing solution was applied to yield a more hydrophilic non-image area and a more lipophilic image area:

Finishing solution for DTR plates	Amount
Gum Arabic (10% in water)	25 ml
Polystyrene sulfonate (20% in water)	100 ml
Citric acid	20 g
1-octyl-5-mercaptotetrazole	2 g
Sodium Hydroxide	5.5 g
Water	1000 g

[0094] The thus obtained printing plate was of good quality with regards to scumming of the non-image area and

dot-quality, and 50000 copies could be obtained.

Example 11 (comparative)

[0095] Molten aluminium (AA1050, alloy composition Al 99.55 wt%, Fe 0.23 wt%, Si 0.17 wt%, Cu 0.010 wt%) was cast according to the DC method into slabs of 450mm x 1200 mm x 3500 mm. These slabs were subjected to 7 mm scalping per surface, soaking at 550 °C for 12 hours, and were then hot-rolled at 500 °C to produce a plate of 5 mm thickness. This plate was cold rolled, annealed at 380 °C for 4 hours, again cold rolled and corrected to yield a coil of aluminium of 0.15 mm thickness.

[0096] The aluminium coil was mechanically grained by a nylon brush and a water suspension of pumice stone 400 mesh). Then, the etching and graining treatment of Example 10 was applied, yielding a centre line average surface roughness R_a of 0.75 μm.

[0097] The thus obtained support was coated with the same photosensitive layers as described in Example 10. The inspection of the coil showed a low number of copper related defects: 2/1000 m^2.

[0098] The plate was exposed, developed and finished in the same way as Example 10.

[0099] Because of the low image strength of parts of the emulsion layer, due to the unevenly distributed Ag nuclei (high amounts in the mechanically induced valleys, low amounts on the tops), only 20,000 copies could be printed.

Example 12 (comparative)

[0100] A support was made in the same way as comparative Example 11, this time omitting the mechanical graining process. The centre line average surface roughness R_a obtained was 0.44 μm.

[0101] After coating the photosensitive layers as described in Example 10, the inspection of the coil revealed a large number of copper related defects: 17/1000 m^2.

Claims

1. Process for producing a digitally imageable lithographic printing plate, comprising forming a support by carrying out the subsequent steps of:

   - continuously casting a molten aluminium alloy to form a strip having a thickness less than 30 mm;
   - cold rolling said strip to form said support;
   - optionally a heat treatment step of said support;
   - correction of the support; and
   - mildly graining said support;

   followed by providing a digitally imageable coating on said support, whereby said printing plate is obtained, wherein said aluminium alloy composition contains iron in an amount of between 0.15% by weight and 0.50% by weight; silicon in an amount of between 0.05% by weight and 0.20% by weight; and copper in an amount of between 0.005% by weight and 0.040% by weight.

2. Process according to claim 1, wherein said aluminium alloy contains iron in an amount of between 0.22% by weight and 0.26% by weight; silicon in an amount of between 0.10% by weight and 0.18% by weight; and/or copper in an amount of between 0.005% by weight and 0.025% by weight.

3. Process according to claim 1 or claim 2, wherein said graining of said support is carried out without any substantial mechanical graining.

4. Process according to any of the previous claims, wherein said graining of the support comprises an electrolytical graining step, preferably using nitric acid or hydrochloric acid as an electrolyte.

5. Process according to any of the previous claims, wherein the continuous casting of the aluminium is carried out using the Hunter method.

6. Process for the production of a digitally imageable lithographic printing plate according to any of the previous claims, wherein the aluminium support has a centre line average surface roughness (R_a) of 0.1 to 0.7 μm.

7. Process for the production of a digitally imageable lithographic printing plate according to any of the previous claims, wherein the aluminium support has a centre line average surface roughness (R_a) of 0.15 to 0.50 μm.

8. Process for the production of a digitally imageable lithographic printing plate according to claim 1-7, which printing plate is sensitive to radiation with a wavelength of between 350 and 1100nm.

9. Process for the production of a digitally imageable lithographic printing plate according to claim 8, which printing plate is sensitive to visible light radiation.

10. Process for the production of a digitally imageable lithographic printing plate according to claim 8, which printing plate is sensitive to infrared radiation.

11. Plate obtainable by the process of any of the previous claims.

FIG. 1(A)

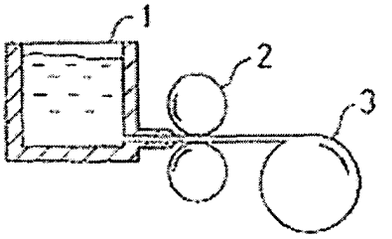


FIG. 1(B)

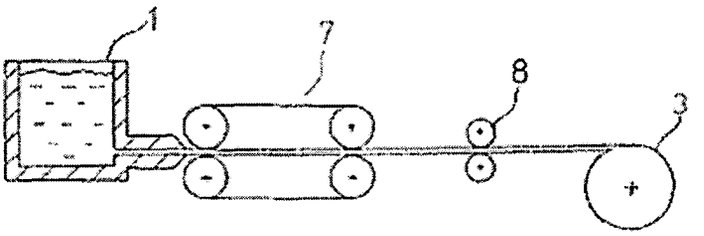


FIG. 1(C)

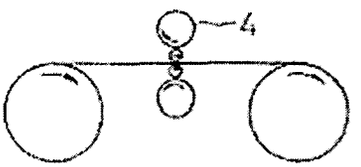


FIG. 1(D)

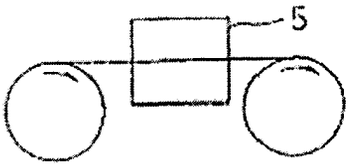


FIG. 1(E)