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(54) Production of support for lithographic printing plate.

(57) A process is provided for the manufacture of a support for a lithographic printing plate precursor, the process comprising treating at least one surface of a metallic substrate with an aqueous solution comprising a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table whilst applying a constant voltage or constant current. Methods are also disclosed for the manufacture of lithographic printing plate precursors which provide plates showing good resistance to abrasion, corrosion, staining and scumming, both on development and on press. Additionally, the plates display excellent coating adhesion in image areas, together with very good exposure latitude and solvent resistance.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a method for the production of a metallic support for use as a substrate for a lithographic printing plate. More specifically, the invention provides a method for the surface treatment of a metallic sheet, most particularly an aluminium sheet, whereby a substrate having particularly favourable lithographic properties may be obtained.

[0002] Conventionally, aluminium substrates intended for use as support materials for lithographic printing plates and their precursors have generally been subjected to surface treatments prior to application of a light sensitive coating material. These treatments serve to improve the lithographic properties of the aluminium, in particular, its hydrophilicity. This is important during printing operations, since the basis of lithography is the ability of the lithographic plate to accept ink in image areas whilst rejecting ink and accepting water in background (non-image) areas, so that the printed image remains free from dirt and other contamination in said background areas. Thus, the light-sensitive coating of a lithographic printing plate precursor is imagewise exposed to radiation in order to change the solubility characteristics of the coating in the radiation-struck areas. The soluble areas are subsequently dissolved away by treatment with a developing solution, to expose the aluminium surface which must be capable of rejecting ink and accepting water.

[0003] A typical surface treatment comprises an initial graining treatment, wherein the aluminium surface is roughened by either mechanical or electrochemical means, and a subsequent anodising treatment, by means of which a layer of aluminium oxide is formed on the surface of the aluminium. Anodising treatments may, for example, be carried out by passing a grained aluminium web through a bath of a suitable anodising acid, such as sulphuric or phosphoric acid, or a mixture thereof, whilst an electric current flows through the anodising bath and the web serves as the anode.

[0004] The presence of a surface anodic layer greatly enhances the hydrophilicity of the aluminium surface, and the adhesion of the subsequently formed image layer is found to be much improved when the surface of the aluminium is subjected to a graining treatment prior to anodising.

[0005] Additionally, there is frequently a requirement for a further surface treatment following the anodising process. Such a treatment - referred to as a post-anodic dip - is generally applied in order to improve specific lithographic printing properties of the substrate, such as clean up of background areas, coating adhesion or corrosion resistance, and will typically involve passing the aluminium through a solution, often an aqueous solution, of the chosen reagent. Commonly used post-anodic dips include aqueous solutions containing, for example, sodium carbonate or bicarbonate, poly(acrylic acid) or various aqueous-soluble copolymers.

[0006] However, whilst conventional anodising and post-anodic dip treatments following graining allow for the production of high quality lithographic substrates, there are clear disadvantages associated with the incorporation of these processes prior to the application of a coating. Both anodising and post-anodic dip solutions are produced in large volumes at elevated temperatures, and this has clear implications in terms of cost, utilisation of space, and subsequent disposal of effluent. In addition to the thermal considerations, the requirement for the passage of an electric current during anodising results in a process requiring a high consumption of energy. Clearly, it would be desirable to provide means whereby this complex series of treatments could be simplified in order to improve the efficiency, and reduce the expense, associated with the preparation of the aluminium substrate. In essence, therefore, it is desirable that the number of substrate treatments required prior to application of the coating should be reduced as far as possible.

[0007] Thus, the present invention seeks to provide a means whereby the costly and time-consuming substrate treatment steps involved in the preparation of suitable aluminium support materials for use in the preparation of lithographic printing plate precursors may be reduced in number and simplified, thereby facilitating substantial cost savings.

[0008] According to the present invention there is provided a process for the manufacture of a support for a lithographic printing plate precursor, said process comprising at least the steps of:

(a) providing a metallic substrate;
(b) treating at least one surface of said substrate with an aqueous solution comprising a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table whilst applying a constant voltage or constant current.

[0009] Said metallic substrate may comprise any conducting metallic substrate but, most preferably, it comprises aluminium or an aluminium alloy containing small amounts of, for example, manganese, nickel, cobalt, zinc, iron, silicon or zirconium. Said substrate is generally provided in the form of a continuous web or roll of metal or metal alloy.

[0010] Preferably, said substrate is subjected to a degreasing treatment prior to said treatment with an aqueous solution of a salt of a metal. Said degreasing treatment is most conveniently carried out by means of an aqueous alkaline solution. Typically, said treatment involves passing said substrate through a bath containing a 5-20% w/v solution of, for example, sodium or potassium hydroxide. Following said degreasing treatment, said substrate is rinsed with water prior to further treatment.

[0011] Said treatment of said surface or surfaces with an aqueous solution comprising a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table is preferably carried out by immersing said substrate in an aqueous solution, preferably containing from 0.001% to 5.0% (w/w) (more preferably from 0.01% to 1.0%) of said salt at a preferred temperature of from 5° to 80°C (more preferably from 15° to 40°C) for a preferred dwell time of from 1 second to 60 minutes (more preferably from 15 seconds to 5 minutes) at a pH of between 0 and 13 (preferably from 1 to 5, and most preferably in the region of 3). Said aqueous solution also preferably contains aluminium ions in an amount of from 0.1 to 50,000 ppm; said aluminium ions may be added to said aqueous solution in the form of any convenient aluminium salt or, in the case of an aluminium substrate, may be present as a result of dissolution from said substrate.

[0012] Suitable salts which may be used for the said treatment include, for example, salts of titanium, zirconium, hafnium, molybdenum, tungsten, vanadium, manganese, nickel, copper, zinc, tin, niobium, tantalum, cerium, selenium, silicon, cobalt or iron. Said salts my include the metal either as the cation, for example in halide, sulphate or nitrate salts, or as part of a complexed anion. Particularly favourable results are achieved with salts of titanium, zirconium or hafnium, such as hafnium sulphate, zirconium phosphate, titanium nitrate, hafnium acetate, zirconium fluoride and titanium chloride. Most preferably, however, the hafnium, zirconium or titanium salt comprises a salt wherein the metal is present in a metal-complex anion, such as a chlorotitanate or fluorozirconate anion. Especially preferred in this regard are the alkali metal fluorozirconates, particularly potassium hexafluorozirconate.

[0013] Optionally, further additives may be incorporated in said aqueous solution containing a metal salt. Preferably, polymers or copolymers of organic acids may be employed for this purpose, with particularly favourable results being achieved with poly(acrylic acid) or the copolymer of acrylic acid with vinyl phosphonic acid. Said materials my be added in an amount of from 0.001% to 5.0% (w/w) (preferably from 0.01% to 1.0%) to the treatment bath.

[0014] The application of the constant voltage or constant current is preferably realised by applying a constant d.c., pulsed d.c., a.c. (sine and square waveforms), biased a.c. or half wave 1-6 phases rectified a.c. voltage of from 0.1 to 1000 V (preferably from 1 V to 100 V) across the treatment bath, using the substrate as one electrode and another electrical conductor, such as platinum, aluminium, carbon, stainless steel or mild steel as the other electrode. Thus, for example, the aluminium substrate may form the cathode and the other electrical conductor may provide the anode; preferably, however, the aluminium substrate forms the anode, with the other electrical conductor providing the cathode. Typically, a.c. current would be supplied at a frequency of from 1-5000 Hz, preferably from 30-70 Hz. The power may be fully applied at the commencement of the electrochemical treatment or, alternatively, can be applied at a progressively increasing rate during the treatment. Following said treatment, a surface film develops on said substrate, said film having a thickness of from 0.001 to 100 µm. Optionally, said surface film may be produced with a textured surface finish.

[0015] Optionally, said substrate may be subjected to a graining treatment prior to said treatment with an aqueous solution of a salt of a metal. Said graining treatment may involve mechanical graining, wherein the surface of the substrate is subjected to mechanical forces which may, for example, be achieved by the use of a slurry of very small metal balls or via brush graining techniques. Alternatively, and most preferably, electrochemical graining may be employed; said technique comprises passing a substrate through a solution of a mineral or organic acid, or a mixture thereof, such as a mixture of hydrochloric and acetic acids, whilst applying an electric current to the acid solution. Typical graining conditions would involve the use of a bath of aqueous hydrochloric acid at a concentration of from 1-10 g/l and a temperature of 5-50°C, with a dwell time of from 1-60 seconds and an applied potential of from 1-40 V. The grained substrate is then rinsed with water prior to further processing.

[0016] Following electrochemical graining, said grained substrate would be subjected to a desmutting treatment in order to remove by-products formed during the course of said electrograining treatment, and deposited on the surface of the substrate. Typically, the process involves treatment of the grained substrate with an aqueous acid or alkali according to the methods well known in the art. The substrate is rinsed with water following desmutting.

[0017] The support provided by the method of the present invention may subsequently be coated with a light-sensitive coating to give a lithographic printing plate precursor.

[0018] Various coatings of the types well known to those skilled in the art may be applied for this purpose, for example, positive-working coatings incorporating quinone diazide derivatives, negative-working coatings incorporating diazo or azide resins or photocrosslinkable resins or silver halide based coatings. The coatings may be applied by any of the standard coating techniques known to the skilled person, such as curtain coating, dip coating, meniscus coating, reverse roll coating, and the like.

[0019] The thus-obtained lithographic printing plate precursor may then be imagewise exposed and the non-image areas can be developed away to provide a lithographic printing plate which is subsequently used on a printing press to produce copies.

[0020] Lithographic printing plates produced from aluminium supports obtained by the method of the present invention show good abrasion resistance, corrosion resistance, staining resistance and scumming resistance, both on plate development and on press. The surface film produced by the treatment according to the method of the present invention shows excellent coating adhesion in the image areas. Additionally, the plate exhibits very good exposure latitude and solvent resistance.

[0021] The inventors have also observed that successful results, in terms of lithographic plate properties, may be achieved by incorporating a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table in a conventional anodising bath, thereby eliminating the requirement for a post-anodic dip treatment. Thus, a salt of this type may be incorporated in an anodising bath typically containing mineral acids such as sulphuric, phosphoric, nitric, hydrofluoric or chromic acids, or organic acids such as oxalic, tartaric, citric, acetic or oleic acids, or mixtures of these acids, thereby providing a support material which shows the advantageous properties previously discussed when incorporated in a lithographic printing plate. Optionally, further additions of materials such as polymers or copolymers of organic acids, typically poly(acrylic acid) or the copolymer of acrylic acid with vinylphosphonic acid, may also be incorporated in the said anodising bath.

[0022] Additionally, the inventors have found that the same advantageous properties are also evident when conventionally grained and anodised aluminium substrate is subjected to the said electrochemical treatment in a solution incorporating a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table, optionally in the presence of further additives, such as polymers or copolymers of organic acids, as previously exemplified. Such a process does not, however, provide all the benefits of reduced processing as previously described, although dwell time is substantially reduced when compared with a standard immersion treatment. Additionally, the resulting substrate shows improved properties when compared with a conventionally grained and anodised substrate which has been subjected to a prior art post-anodic dip treatment.

[0023] The invention will now be illustrated, though without limitation, by reference to the following examples:

EXAMPLES

Example 1

[0024] A conventionally degreased, grained and desmutted aluminium substrate was immersed for 120 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of potassium hexafluorozirconate (5 g/l) at room temperature. A constant d.c. voltage of 15 V was applied across the carbon electrode and the aluminium electrode which was formed by the aluminium substrate, the carbon electrode serving as the cathode and the aluminium electrode as the anode.

[0025] The resulting substrate was rinsed with water and coated with a solution of a naphthoquinone diazide photosensitive resin and a cresol novolak support resin in 2-methoxypropanol to produce a light-sensitive coating layer, and the coated substrate was baked at 130°C for 5 minutes. The resulting lithographic printing plate precursor was imagewise exposed to UV light at 100-300 mJ/cm^2 and the non-image areas were developed away with an aqueous alkaline developer solution by immersion for 30 seconds at 20°C. The resulting lithographic printing plate was rinsed with water and dried in a stream of cool air and subsequently produced 250,000 excellent quality copies on a Drent Web Offset press. The plate showed excellent resistance to abrasion, corrosion and staining/scumming, both during development and on press.

Example 2

[0026] A conventionally degreased aluminium substrate was immersed for 10 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of potassium hexafluorozirconate (5 g/l) at room temperature. A constant d.c. voltage of 15 V was applied across the carbon electrode and the aluminium electrode which was formed by the aluminium substrate, the carbon electrode serving as the cathode and the aluminium electrode as the anode.

[0027] The resulting substrate was coated, baked, exposed and developed in exactly the same manner as described for Example 1 to provide a lithographic printing plate which produced 250,000 excellent quality copies on a Drent Web Offset press. The plate showed excellent resistance to abrasion, corrosion and staining/scumming, both during development and on press.

Example 3

[0028] A conventionally degreased, grained, desmutted and anodised aluminium substrate was immersed for 5 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of potassium hexafluorozirconate (5 g/l) at room temperature. An a.c. voltage of 15 V was applied across the carbon electrode and the aluminium electrode which was formed by the aluminium substrate, the carbon electrode serving as the cathode and the aluminium electrode as the anode.

[0029] The resulting substrate was coated, baked, exposed and developed in exactly the same manner as described for Example 1 to provide a lithographic printing plate which produced 250,000 excellent quality copies on a Drent Web Offset press. The plate showed excellent resistance to abrasion, corrosion and staining/scumming, both during development and on press.

Example 4

[0030] A conventionally degreased, grained and desmutted aluminium substrate was immersed for 120 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of zirconium sulphate (5 g/l) at room temperature. A rectified a.c. voltage of 15 V was applied across the carbon electrode and the aluminium electrode which was formed by the aluminium substrate, the carbon electrode serving as the cathode and the aluminium electrode as the anode.

[0031] The resulting substrate was coated, baked, exposed and developed in exactly the same manner as described for Example 1 to provide a lithographic printing plate which produced 250,000 excellent quality copies on a Drent Web Offset press. The plate showed excellent resistance to abrasion, corrosion, and staining/scumming, both during development and on press.

Claims

1. A process for the manufacture of a support for a lithographic printing plate precursor, said process comprising at least the steps of:

(a) providing a metallic substrate;

(b) treating at least one surface of said substrate with an aqueous solution comprising a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table whilst applying a constant voltage or constant current.

2. A process as defined in claim 1 wherein said metallic substrate comprises aluminium or an aluminium alloy containing small amounts of at least one of manganese, nickel, cobalt, zinc, iron, silicon or zirconium.

3. A process as defined in claim 1 or 2 wherein said salt comprises a salt of titanium, zirconium, hafnium, molybdenum, tungsten, vanadium, manganese, nickel, copper, zinc, tin, niobium, tantalum, cerium, selenium, silicon, cobalt or iron.

4. A process as defined in any of claims 1-3 wherein said salt includes the metal as the cation.

5. A process as defined in claim 4 wherein said salt comprises the sulphate, phosphate, nitrate, acetate, fluoride or chloride salt of titanium, zirconium or hafnium.

6. A process as defined in any of claims 1-3 wherein said salt includes the metal as part of a complexed anion.

7. A process as defined in claim 6 wherein said salt comprises an alkali metal fluorozirconate.

8. A process as defined in claim 7 wherein said alkali metal fluorozirconate comprises potassium hexafluorozirconate.

9. A process as defined in any preceding claim wherein said aqueous solution additionally includes a polymer or copolymer of an organic acid.

10. A process as defined in claim 9 wherein said polymer or copolymer comprises poly(acrylic acid) or the copolymer of acrylic acid with vinylphosphonic acid.

11. A process as defined in any preceding claim wherein said aqueous solution aluminium ions in an amount of from 0.1 to 50,000 ppm.

12. A process as defined in any preceding claim wherein said aqueous solution contains from 0.001% to 5.0% (w/w) of said salt.

13. A process as defined in any preceding claim wherein said treatment is carried out at a temperature of from 5° to 80°C.

14. A process as defined in any preceding claim wherein said treatment is carried out for a dwell time of from 15 seconds to 5 minutes.

15. A process as defined in any preceding claim wherein said treatment is carried out at a pH of from 1 to 5.

16. A process as defined in any preceding claim wherein said application of constant voltage or constant current is realised by applying a constant d.c., pulsed d.c., a.c. (sine or square waveform), biased a.c. or half wave 1-6 phases rectified a.c. voltage of from 0.1 to 1000V across the treatment bath.

17. A process as defined in claim 16 wherein said a.c. current is applied at a frequency of from 30-70 Hz.

18. A process as defined in claim 16 or 17 wherein the substrate comprises one electrode and platinum, aluminium, carbon, stainless steel or mild steel comprises the other electrode.

19. A process as defined in claim 18 wherein said substrate comprises aluminium and forms the anode.

20. A process as defined in any preceding claim wherein said substrate is subjected to a degreasing treatment prior to said treatment with an aqueous solution of a salt of a metal.

21. A process as defined in claim 20 wherein said degreasing treatment is carried out by means of an aqueous alkaline solution.

22. A process as defined in any preceding claim wherein said substrate is subjected to a graining treatment prior to said treatment with an aqueous solution of a salt of a metal.

23. A process as defined in claim 22 wherein said substrate is subjected to a desmutting treatment following said graining treatment.

24. A method for the manufacture of a lithographic printing plate precursor which comprises the steps of:

(a) providing a support for said precursor according to a process as defined in any preceding claim;

(b) applying a light sensitive coating to the treated surface or surfaces of said support.

25. A method for the manufacture of a lithographic printing plate precursor which includes the step of treating a substrate comprising aluminium or its alloy in an anodising bath comprising:

(a) a mineral acid or an organic acid or a mixture thereof; and

(b) a salt of a metal from Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table.

26. A method for the manufacture of a lithographic printing plate precursor which includes the step of treating a grained and anodised substrate comprising aluminium or its alloy in an aqueous solution comprising a salt of a metal front Group IB, IIB, IVA, IVB, VB, VIA, VIB, VIIB or VIII of the Periodic Table whilst applying a constant voltage or a constant current.