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(71) Applicant: **AGFA-GEVAERT N.V.**

**2640 Mortsel (BE)**

(72) Inventors:

- **Chau, Tu Vinh**  
**Leeds, Yorkshire LS14 1AP (GB)**
- **Mayers, Felton Rudolph**  
**Leeds, Yorkshire LS17 5DF (GB)**

(54) **Production of lithographic printing plate support**

(57) A process is provided for the manufacture of a support for a lithographic printing plate precursor, the process comprising graining at least one surface of a metallic substrate, applying an anodic layer to at least one grained surface of the substrate, and treating at least one grained and anodised surface of the substrate with an aqueous solution comprising a copolymer of acrylic acid and vinylphosphonic acid whilst applying a constant voltage or constant current. A method is 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 con-

taining, for example, sodium carbonate or bicarbonate, poly(acrylic acid) or various aqueous-soluble copolymers.

**[0006]** Conventionally, the application of a post-anodic dip has been carried out by simple dipping of the grained and anodised substrate in the manner just described. However, the present inventors have now surprisingly found that significantly improved plate properties can be obtained by carrying out the aforesaid treatment using a dipping agent comprising a copolymer of acrylic acid and vinylphosphonic acid whilst, during the course of the dipping treatment, applying electrical forces to the system. In this way, plates showing significantly improved clean up properties, enhanced run length and excellent corrosion resistance can be produced.

**[0007]** Thus, 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 the steps of:

- (a) providing a metallic substrate;
- (b) graining at least one surface of said substrate;
- (c) applying an anodic layer to at least one grained surface of said substrate; and
- (d) treating at least one grained and anodised surface of said substrate with an aqueous solution comprising a copolymer of acrylic acid and vinylphosphonic acid whilst applying a constant voltage or constant current.

**[0008]** 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.

**[0009]** Preferably, said substrate is subjected to a degreasing treatment prior to said graining treatment. 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.

**[0010]** Said treatment of said grained and anodised surface or surfaces with an aqueous solution comprising a copolymer of acrylic acid and vinylphosphonic acid 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 copolymer 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.

**[0011]** Said copolymer of acrylic acid and vinylphosphonic acid may be prepared by any of the standard polymerisation techniques known in the art, for example solution polymerisation, suspension polymerisation or emulsion polymerisation. Copolymers which are suitable for use in the method of the present invention typically have a weight average molecular weight in the range of from 10000 to 100000, preferably from 30000 to 70000, and most preferably in the region of 50000; the ratio of acrylic acid units to vinylphosphonic acid units in the copolymers typically lies in the range of from 0.5:1 to 1.5:1, preferably from 0.85:1 to 1.30:1.

**[0012]** 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 1v 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 1 to 500 nm. Optionally, said surface film may be produced with a textured surface finish.

**[0013]** The graining treatment carried out in accordance with the method of the present invention 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.

**[0014]** Following electrochemical graining, said grained substrate is preferably 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.

**[0015]** The grained and optionally desmuted substrate is then subjected to an anodising treatment in order to provide an anodic film of aluminium oxide on the grained surface or surfaces of the substrate. Anodising methods are well known in the art and typically involve passing the substrate through a bath containing an aqueous mineral acid, such as sulphuric, phosphoric, nitric, hydrofluoric or chromic acid, or an aqueous solution of an organic acid, for example oxalic, tartaric, citric, acetic or oleic acid, or a mixture of these acids, whilst applying an electric current to the anodising bath. Typical anodising conditions would involve the use of a bath of sulphuric acid at a concentration of from 10 to 300 g/l, preferably in the region of 120 g/l, and a temperature in the range of from 20°-60°, preferably in the region of 40°C, with a dwell time of from 5 to 120 seconds, preferably around 40 seconds, an applied potential of from 10-25 V, preferably about 20 V, and a current density of from 1000-2000 A/m<sup>2</sup>, preferably in the region of 1400 A/m<sup>2</sup>. The grained and anodised substrate is then rinsed with water prior to further processing.

**[0016]** 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.

**[0017]** 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.

**[0018]** 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.

**[0019]** Lithographic printing plates produced from aluminium supports obtained by the method of the present invention show excellent 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, and its overall properties are significantly improved when compared with a grained and anodised substrate which has been subjected to a prior art post-anodic dip treatment.

[0020] The invention will now be illustrated, though without limitation, by reference to the following examples:

## EXAMPLES

### Example 1

[0021] A conventionally degreased, grained, desmuted and anodised aluminium substrate was immersed for 120 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of a copolymer of acrylic acid and vinylphosphonic acid (1:1) ( $M_w$  50000) (10 g/l) at room temperature. A constant d.c. voltage of 60 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.

[0022] 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<sup>2</sup> 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

[0023] A conventionally degreased, grained, desmuted and anodised aluminium substrate was immersed for 10 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of a copolymer of acrylic acid and vinylphosphonic acid (1:1) ( $M_w$  50000) (10 g/l) at room temperature. An a.c. voltage of 10 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.

[0024] 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 cop-

ies 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

[0025] A conventionally degreased, grained and desmuted aluminium substrate was immersed for 120 seconds in a bath fitted with a carbon electrode, and containing an aqueous solution of a copolymer of acrylic acid and vinylphosphonic acid (0.9:1) ( $M_w$  55000) (5 g/l) at room temperature. A rectified a.c. voltage of 20 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.

[0026] 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 the steps of:
  - (a) providing a metallic substrate;
  - (b) graining at least one surface of said substrate;
  - (c) applying an anodic layer to at least one grained surface of said substrate; and
  - (d) treating at least one grained and anodised surface of said substrate with an aqueous solution comprising a copolymer of acrylic acid and vinylphosphonic acid 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 copolymer of acrylic acid and vinylphosphonic acid has a weight average molecular weight in the range of from 10,000 to 100,000.
4. A process as defined in claim 3 wherein said weight average molecular weight is in the region of 50,000.

5. A process as defined in any preceding claim wherein the ratio of acrylic acid units to vinylphosphonic acid units in said copolymer lies in the range of from 0.5:1 to 1.5:1.
6. A process as defined in claim 5 wherein said ratio of acrylic acid units to vinylphosphonic acid units lies in the range of from 0.85 to 1.30:1.
7. A process as defined in any preceding claim wherein said aqueous solution additionally contains aluminium ions in an amount of from 0.1 to 50,000 ppm.
8. A process as defined in any preceding claim wherein said aqueous solution contains from 0.001% to 5.0% (w/w) of said copolymer.
9. A process as defined in any preceding claim wherein said treatment is carried out at a temperature of from 5° to 80°C.
10. 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.
11. A process as defined in any preceding claim wherein said treatment is carried out at a pH of from 1 to 5.
12. 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.
13. A process as defined in claim 12 wherein said a.c. current is applied at a frequency of from 30-70 Hz.
14. A process as defined in claim 12 or 13 wherein the substrate comprises one electrode and platinum, aluminium, carbon, stainless steel or mild steel comprises the other electrode.
15. A process as defined in claim 14 wherein said substrate comprises aluminium and forms the anode.
16. A process as defined in any preceding claim wherein said graining treatment comprises electrochemical graining.
17. A process as defined in claim 16 wherein said electrochemical graining comprises passing said substrate through a solution of a mineral or organic acid or a mixture thereof whilst applying an electric current thereto.
18. A process as defined in claim 17 wherein said solution comprises a mixture of hydrochloric acid and acetic acid.
19. A process as defined in claim 17 or 18 wherein said substrate is subjected to a desmutting treatment following said electrochemical graining treatment.
20. A process as defined in any preceding claim wherein said anodic film is applied to said grained surface or surfaces of said substrate by passing said substrate through a bath containing aqueous mineral or organic acid or a mixture thereof whilst applying an electric current thereto.
21. A process as defined in claim 20 wherein said bath contains sulphuric acid.
22. A process as defined in any preceding claim wherein said substrate is subjected to a degreasing treatment prior to said graining treatment.
23. A process as defined in claim 22 wherein said degreasing treatment is carried out by means of an aqueous alkaline solution.
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 of surfaces of said support.