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

(11) EP 0 798 130 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
07.06.2000 Bulletin 2000/23

(51) Int Cl.[7]: **B41N 3/03**

(21) Application number: **97200794.2**

(22) Date of filing: **17.03.1997**

(54) **Lithographic plates with coating**

Flachdruckplatten mit Beschichtung

Plaques lithographiques avec revêtement

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **29.03.1996 EP 96200865**

(43) Date of publication of application:
01.10.1997 Bulletin 1997/40

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- **DATABASE WPI Week 8619 Derwent Publications Ltd., London, GB; AN 86-123162 XP002011545 & JP 61 063 497 A (KOBE STEEL KK)**
- **DATABASE WPI Week 8815 Derwent Publications Ltd., London, GB; AN 88-103036 XP002011546 & JP 63 054 287 A (RICOH KK)**
- **DATABASE WPI Week 8716 Derwent Publications Ltd., London, GB; AN 87-113678 XP002011547 & JP 62 060 695 A (RICOH KK)**

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Description

1. Field of the invention.

[0001] This invention concerns a lithographic plate support. A lithographic plate support comprises a substrate, typically of steel, aluminum, plastic or paper, carrying a surface coating whose properties are critical. This invention concerns the provision of improved surface coatings.

2. Background of the invention.

[0002] Lithographic printing processes rely on the differential wetting characteristics of hydrophobic and hydrophilic surfaces. When aluminum sheets are used as substrates, in practice an aluminum surface is roughened, anodised, conditioned and then coated with a light-sensitive coating. Positive and negative images are normally formed on the surface of the printing plate by photographic methods. Development of the image results in removal of the organic coating from either the exposed or unexposed areas. The organic areas are oleophilic and will accept oil-based inks but will not water wet. In contrast, the conditioned anodic oxide has a surface energy and can accept either water or ink, however, when wet it will not accept ink. In conventional practice, the roughening stage is critical for print quality and requires uniform topographies with surface features in the range of 0.01 - 4 μm. The actual range employed for any particular plate depends predominantly on the quality of paper and required print finish. It is common practice, when very long print runs are required, to bake the plate (after developing) to above 200°C. This treatment enhances the interaction between organic and oxide layers.

[0003] The most common method of achieving the high standard of roughening required for lithographic plates is to electrochemically treat the surface. However, the process has several limitations. Specifically, it can only be run at low speeds and it requires very high quantities of electrical power and the use of specialist materials. Production of these materials demands special and costly practices in order to ensure the high quality of the final product. Also, expensive waste treatment plant is required to treat the waste chemicals from anodising and graining aluminum.

[0004] The usual practice is then to anodise the roughened surface, in order to provide an anodic oxide coating having suitable water-wetting ink-wetting properties. Like the roughening process, the anodising process is relatively slow and expensive.

[0005] It is known to prepare a lithographic printing plate by applying to a substrate a suspension or sol of preformed particles, and removing the liquid to leave a coating comprising the particles. The particles may be bound together by means of a polymer or by partial sintering, but organic polymers may affect the hydrophilic lipophilic balance of the surface while partial sintering may require heating to such high temperatures as to damage the substrate.

[0006] WO 91/12140 (Alcan International Limited) describes a lithographic plate comprising a substrate carrying an oxide layer derived from a Type A sol. The substrate may be metal, e.g. aluminum or steel, and may be in a mill finish state or grained or otherwise profiled. The sol may include an inorganic passenger powder which may impart a desired topography to the coating layer.

[0007] US 3,971,660 describes a lithographic plate comprising a support having a hydrophilic surface comprising the homogeneous reaction product of hydrolysed polyvinyl acetate and hydrolysed tetraethyl orthosilicate.

[0008] US 3,608,489 describes a lithographic plate comprising a support coated with a reaction product of a water soluble urea- or melamineformaldehyde resin and a water soluble colloid containing free acids groups. Said coating can contain titanium dioxide or silica.

[0009] US 3,298,852 describes a lithographic plate comprising a support which is treated with a solution containing polyacrylic acid.

[0010] JP 61/63 497 describes a lithographic plate comprising a support coated with a mixture of e.g. styrene-maleic acid copolymer and silicate.

[0011] US 3,912,548 describes contacting a metal surface with an aqueous composition consisting of a soluble zirconium compound and a polymeric materiale.g. polyacrilic acid.

[0012] JP 63/54287 describes a lithographic plate comprising an image receiving layer comprising inorganic pigment containing alumina and a water soluble binder.

[0013] JP 62/60695 describes a lithographic plate including silicaalumina colloidal pigment and a hydrophilic binder e.g. polyacrylate.

[0014] US 4,046,946 describes a lithographic printing surface wherein said surface comprises a coating of colloidal silica and insolubilized hydrophilic polymer. Polycarboxy organic polymers are not mentioned herein.

[0015] US 3,922,441 describers a lithographic printing plate comprising a lithographic printing surface, said surface comprising a coating of colloidal silica and insolubilized hydrophilic polymer. Polycarboxy organic polymers are not mentioned herein.

[0016] DE 1,210,437 describes a lithographic printing plate which comprises a dried hydrophilic, in water insoluble layer consisting of polyacrylic acid resin and zinc oxide.

3. Summary of the invention.

[0017] It is an object of the present invention to provide a lithographic support having excellent printing characteristics.

[0018] Further objects of the present invention will be-

come clear from the description hereafter.

[0019] In one aspect, the invention provides a lithographic plate support comprising a substrate and a coating thereon derived from an aqueous composition comprising an inorganic sol or metal salt solution and a polycarboxy organic polymeric material wherein the metal salt or the oxide of the inorganic sol within the aqueous composition are capable of cross-linking and making insoluble the polycarboxy organic polymeric material characterized in that the thickness of said coating is at least 30 nm.

[0020] In a preferred embodiment, the invention provides a lithographic plate support comprising a substrate and a coating thereon derived from a coating composition consisting of basic units which are polynuclear ions selected from the group Al(III) Fe(III), Zr(IV) Th(IV) Ce(IV) Ti(IV) forming an inorganic polymer.

4. Detailed description of the invention.

[0021] An essential component of the coating on the substrate is a polycarboxy organic polymeric material. Examples of polycarboxy organic polymeric materials include polyacrylic acid, polymethacrylic acid, polyethylacrylic acid, polydimethylaminoethylene acrylic acid and also co- and terpolymers of these monomeric constituents. These materials are typically soluble, or at least readily emulsifiable, in water.

[0022] The coating applied to the substrate constitutes a key feature of one aspect of the invention. The coating is derived from an aqueous composition comprising an inorganic sol or metal salt solution and a polycarboxy organic polymeric material wherein the metal salt or the oxide of the inorganic sol within the aqueous composition are capable of cross-linking and making insoluble the polycarboxy organic polymeric material characterized in that the thickness of said coating is at least 30 nm. Aqueous sols can be classified in three categories, Type A, Type B and Type C.

[0023] Type A sols consist of basic units which are polynuclear ions which form an 'inorganic polymer' and are formed by hydrolysis and polymerisation of monomeric cations. The molecular weight of the polynuclear cations will depend on the degree of hydrolysis but these sols normally have an anion to metal ratio of approximately 1:1. The polymeric species are not large enough to scatter light efficiently, so the sol and the resultant gel are optically clear. The gel has a high density, low porosity and the X-ray diffraction pattern consists of very broad bands. See J. D. F. Ramsay "Neutron and Light Scattering Studies of Aqueous Solutions of Polynuclear Ions. Water and Aqueous Solutions", 207-218 1986 (ed G.W. Neilson and J. E. Enderby; Bristol. Adam Hilger). Type A sols may be formed from the polynuclear ions listed in this paper including those containing Al(III) Fe (III) Zr(IV) Th(IV): for example: $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$.

[0024] Type B sols consist of basic units or particles with a definite shape, e.g. spherical, rod or plate-like, and which are amorphous or microcrystalline. The sol is formed by extensive hydrolysis of a salt and has a low anion to metal atom ratio of approximately 0.3:1. The sols can also be prepared by peptization of fresh precipitates. The colloidal units are not aggregated and the sol and the resultant gel may both be clear. Type B sols include Al(III) Zr(IV) Ce(IV) Ti(IV) Fe(III). Preparation of Type B Al(III) sols is described in GB 1.174.648. Preparation of Ce Type B sol is described in GB 1.342.893. Type B alumina sols are available commercially.

[0025] In the type C sol the basic colloidal units are aggregated. They are crystalline and the gels formed by removal of water have a low density. These sols scatter light and are therefore opaque. The sols formed from ultrafine powders prepared by vapour phase techniques, i.e. flame hydrolysed powders, belong to this category.

[0026] Type A and B sols when dehydrated yield gels which are >45 % of the theoretical density of the oxide. The gels derived from a type C sol are porous and have a density of <45 % of the theoretical density of the oxide.

[0027] The inorganic sol for use in this invention is preferably a hydrous oxide sol, e.g. a hydrous metal oxide sol, that is to say a Type A sol. Examples are zirconia sols, ceria sols, titania sols, hafnia sols, alumina sols, and iron oxyhydroxide sols. Silica sols exemplify non-metal oxide sols.

[0028] Zircona Type A sols are readily formed by peptising basic zirconium carbonate in mineral acid. The constitution of zirconia sols when the associated anion is nitrate or bromide or chloride is discussed in a UKAEA Research Group Report, reference AERE - R5257 (1966) by J. L. Woodhead and J. M. Fletcher. Zirconia sols contain extensively hydrolysed inorganic polymers with a primary particle size of less than 10 nm. The polymer is thought to be built up of hydrated oxyhydroxide species of zirconium. When nitric acid is used, the species is believed to have the formula:

$$[Zr_4(OH))_{12}(NO_3)_2(H_2O)_4]_n\ (NO_3)_{2n}.2nH_2O,$$

where n is thought to be approximately one in dilute sols and greater than one at higher concentrations.

[0029] MEL Chemicals sells Type A sols based on ammonium zirconyl carbonate under the Trade Marks AZC and BACOTE 20, the latter including a tartaric acid stabiliser.

[0030] Alumina type A sols may be prepared by denitration of an aqueous aluminum nitrate solution using an organic water-immiscible amine such as that sold under the Trade Mark Primene JMT.

[0031] Type A sols can also be formed by controlled hydrolysis of metal alkoxides. The alkoxide is provided in solution in an organic solvent, and a controlled amount of water added to form polynuclear cations. The same technique is available for forming type A silica sols from organic solutions of alkoxysilanes. However, this

route is unsatisfactory; organic groups may need to be removed from the coating; organic solutions are a fire hazard. The Type A sols used in this invention are preferably derived from inorganic precursors (including carbonates).

[0032] On gelling Type A sols, the polynuclear cations polymerise by a chemical reaction to form a crosslinked inorganic network. By contrast on gelling type B or type C sols, the sol particles merely aggregate or physically fuse together. As a result, coatings formed from type A sols are more coherent than those formed from type B or type C sols, and without the need to cure at temperatures high enough to sinter the particles.

[0033] Ceria and titania and other hydrous metal oxide Type A sols may be formed by peptising the corresponding hydrated metal oxide with a mineral acid.

[0034] The nature of the substrate is not critical. Substrates which are conventionally used for lithographic plates may be used in this invention. The most preferable substrate is an aluminum sheet, but other metals including steel are used, as are plastics sheet, metallised plastics and even paper. Metal substrates may carry a continuous electroplated coating, e.g. of nickel or chromium. The aluminum or steel or other substrate may have a grained or profiled surface, but it is an advantage of the invention that the substrate may be used in a mill finished state or otherwise as supplied, without the need for special surface profiling; a wide range of Al alloys is thus possible. For example, the required lithographic plate support strength may be obtained by the use of a thinner sheet of a higher alloyed composition.

[0035] An aqueous composition may be formed by combining a Type A hydrous oxide sol with a polycarboxy organic polymeric material either in aqueous solution or emulsion. When this aqueous composition is applied to a substrate and dried thereon to form a coating, it is believed that the metal or other oxide of the sol acts to cross-link and thus insolubilise the polycarboxy organic polymeric material. In a preferred example, the polycarboxy organic polymeric meterial is polyacrylic acid, and the sol is a Type A zirconia sol with the zircona acting to cross-link the polyacrylic acid through the carboxyl groups. Cross-linking of the polycarboxy organic polymeric material reduces the water sensitivity of the coating and permits increased print runs.

[0036] The polycarboxy organic polymeric material can be a homo- or copolymer, with one or more repeating groups selected from the group consisting of acrylic, methacrylic, itaconic, mesaconic and citraconic acid, further alkyl substituted acrylic acids with alkyl radicals having 2 to 6 carbon atoms, half ester of α, β-unsaturated vinylidene dicarboxylic acids having from 4 to 12 carbon atoms in the acid moiety, the alcanol groups being selected from linear and branched saturated and unsaturated hydrocarbons having 1 to 20 carbon atoms, and dialkylamino alkyl acrylic acid having from 6 to 20 carbon atoms.

[0037] In these coating compositions, and in coatings formed from them, ZrO_2 or other metal oxides derived from the sol and polyacrylic acid or other polycarboxy organic polymeric material, are preferably present in proportions by weight in the range 99.5/0.5 to 0.5/99.5, particularly 20:1 to 1:20. As the examples below show, addition of as little as 1 % of polyacrylic acid to 99 % of sol generates a noticeable improvement; while at the other end of the range, polyacrylic acid has useful properties as a coating, even in the complete absence of any sol or metal salt solution. It may be convenient to gel the sol, either before or after application of the aqueous composition to form a coating on the substrate. Known chemical techniques for gelling Type A sols can be used.

[0038] The aqueous composition may also contain a powder which can be used to give the coating on the substrate a desired surface topography.

[0039] When used, the powder is preferably an inert metal oxide such as silica, zirconia, titania or alumina. This may be a type C sol, or a powder produced by comminution, for example. Powder loadings of 1 to 300 gl^{-1}, preferably 5-150 gl^{-1}, more particularly 10-75 gl^{-1} are appropriate. The powder may have an average particle size below 10 μm, preferably below 5 μm, e.g. in the range 3-500 nm, and is preferably of substantially uniform particle size. When a fluid brings about gelation of the sol, the powder becomes incorporated in the layer on the substrate surface.

[0040] However, the use of particulate material can give rise to difficulties, and it has been found in general not necessary in this invention. This finding is rather surprising. Conventional wisdom has it that a lithographic support needs to be rough in order to bond firmly an overlying light-sensitive layer of the lithographic plate. With the coatings of this invention, such roughness is in general not necessary.

[0041] The zirconia sol/polyacrylic acid system is not in itself new, for it has been widely described for coating metal and other substrates in order to improve their adhesion to subsequently applied organic layers such as paint, varnish and adhesive. One such publication is U. S. patent 3,912,548 (Faigen, 1975). But the properties required of an adhesion-promoting coating are quite different from those required for a lithographic support coating. In that aspect the thickness of the coating containing the zirconia sol/polyacrylic acid system has never been defined. The advantageous print properties demonstrated in the examples below could not have been predicted from the known adhesion-promoting properties of such coatings in the prior art.

The surface to which the coating is to be applied may be cleaned by conventional means appropriate to the substrate concerned. For aluminum this may be an acid or alkaline cleaning treatment, using commercially available chemicals such as those sold by ICI under the Trade Marks Ridolene 124 and 124E. Alternatively, the metal surface may be pretreated to form thereon an artificially applied oxide layer. Such treatments include acid etching (Forest Product Laboratories) and anodising

treatment with sulphuric, chromic or phosphoric acid. However, these pretreatments are quite expensive, and are preferably omitted as unnecessary for lithographic supports according to this invention.

[0042] The composition may be applied to the substrate surface (optionally carrying a profiled surface) by any convenient technique, such as spin coating, immersion, flow or roller coating, brushing, or by spraying. For aluminum strip, roller coating is likely to be an attractive option. The formulation may need to be adjusted to provide a convenient viscosity for application by the desired method. After application and drying, the coating on the surface may be cured. Curing temperatures are from ambient up to the decomposition temperature of the hydrophilic organic polymeric material, usually (though not always) below those required to fully sinter the particles, and are preferably in the range 50 to 400 °C at which the substrate is stable, more preferably in the range 100 °C to 350 °C. Removal of water takes place progressively and is still not complete at 400 °C.

[0043] The substrate surface preferably carries the coating at a thickness of at least 30 nm, preferably of at least 50 nm and most preferably of at least 75 nm. The maximum thickness of the coating is not so important but is preferably less than 4 μm, more preferably less than 2.5 μm, most preferably less than 1 μm. If more pronounced surface texture is required, thicker coatings, e.g. of up to 5 gm^{-2} may be preferred and passenger powders with average particle sizes up to 1 micron or even up to 10 microns may be used. The invention envisages as an additional method step the application to the coating layer of one or more subsequent layers, such as are conventional in lithography.

[0044] A lithographic plate may carry an image-forming layer, or, alternatively a radiation-sensitive or photosensitive layer, respectively, overlying the coated substrate support. Photosensitive image-forming layers are well known in the art. They may be applied by the manufacturer before distribution; or by the user by a wipe-on technique before use. The lithographic plate is exposed to light and then developed in order to obtain a printing plate. Preferably said printing plate is after the development subjected to a baking step. Said baking can proceed at temperatures from 100 °C to 250 °C for a time of 40 minutes to 1 minute. Depending on the chemistry of the photosensitive layer, either that portion which has been exposed to light, or, alternatively that portion which has not been exposed to light, may be removed.

[0045] A lithographic support is required to firmly bond that portion of the image-bearing layer that is to be present during printing; but to readily release that portion of the image layer that is not present during printing. As described in the examples below, printing trials have demonstrated that lithographic plates according to the invention have excellent properties in this respect. The lithographic plates used in the examples do not have the grained surface conventionally present on aluminum lithographic plates, and this may be an advantage in permitting better print definition.

EXAMPLE 1 (according to the invention)

Sol-gel Formulation

[0046] 4.2 g of a 25 wt% solution (1.05 g PAA equivalent) of polyacrylic acid (Trade name Acumer 1510 from Rohm & Haas) was added to 100 g of water, and stirred. 5.2 g of a 20 wt% solution (1.04 g ZrO_2 equivalent) of ammonium zirconium carbonate (Trade name Bacote 20) was added, and the mixture stirred to produce the coating solution. The preparation can be scaled-up to produce larger quantities; ten litres of solution has been produced in a single batch for trials.

Metal cleaning

[0047] Three methods of cleaning lithographic sheet prior to coating have been used; caustic, phosphoric acid and sulphuric acid. A preferred method is caustic cleaning (followed by a nitric acid desmut). A technical benefit may be obtained by cleaning in phosphoric acid. Zirconium species in solution are known to bind strongly with phosphate groups, thus the phosphoric acid clean (which leaves residual phosphate groups on the cleaned surface) may improve coat adhesion and abrasion resistance. Sulphuric acid was used in a trial to assess large scale production methods.

1. Caustic cleaning

Caustic clean/etch

[0048] A solution of 20 gl^{-1} NaoH at 60 °C - the plates are immersed for 60 seconds, which exceeds the required cleaning time, but the surface etching provides a matt finish which may be a property desired by the printers. The plates are rinsed with water.

Nitric acid desmut

[0049] A solution of 12 gl^{-1} HNO_3 at room temperature - the plates are immersed for 60 seconds, which again exceeds the "normal" desmut requirements. The additonal cleaning time increases the quantity of intermetallics on the metal surface, thus the desmut time is increased to ensure adequate removal. The plates are rinsed with water, and allowed to air dry prior to coating.

2. Phosphoric Acid Cleaning

[0050] A solution of 20 wt/vol% (i.e. 20 g of concentrated H_3PO_4 is diluted to a total volume of 100 ml) at 90°C. The plates are immersed for 60 seconds, then rinsed with water and allowed to air dry prior to coating.

3. Sulphuric/hydrofluoric Acid Cleaning

[0051] During a line trial to assess the feasibility of coating with zirconia:polyacrylic acid on a large scale, a coil of aluminum was cleaned in a continuous web. The metal passed through cleaning baths containing sulphuric acid (1.1 wt%) and hydrofluoric acid (80 ppm). The bath temperature was 70°C and immersion time was 12 s.

Coating and Curing

[0052] Samples produced for coating optimisation and print trials are produced by spin coating, but it is envisaged that full-scale production will be achieved by roller coating a coil of aluminum. The coating solution described above, unlike some commercial pretreatment solutions, does not contain any aggressive chemical reagents such as hydrofluoric acid, which provide a degree of cleaning. It is therefore important to coat the plates as soon as possible after cleaning. The coating thickness is tailored by controlling the solution concentration and the spin speed. The coating thickness has not been fully optimised, but it is known that the thickness used in pretreating the metal (typically <25 nm) provide insufficient abrasion resistance to use as lithographic plates. Three coating thicknesses (75-150 nm) have been submitted for full print evaluation. The plates are spun at a pre-defined speed (depositing a known film thickness), and the coating solution is applied from the centre of the plate, moving outwards to the edges. The plate is spun for a further 60 seconds after the solution has been applied. The plates are stored flat, and allowed to air dry. The plates are then inserted into a pre-heated oven (180°C) for 60 seconds, and allowed to cool.

[0053] Light-sensitive coatings are then applied (these can be either positive or negative coatings) by spin coating, and the coating is image-wise cured by exposing through a mask and developed. This produces an image on the plate; the image area is ink-wetted, and the non-image area (the sol-gel film) is water-wetted.

[0054] Plates produced by this additive graining technique have been evaluated in print trials, but these have been limited in run length to 30,000 impressions. The results have been compared with the performance of "standard" anodised lithographic plate. The results are as follows:

- Light sensitivity - better than standard
- Light sensitive coating - better than standard
- Water consumption - better than standard
- Run-up procedure - better than standard
- Contrast after developing - better than standard
- Screen reproduction - ok
- Film edges - ok
- Contrast after exposing - ok

[0055] The subjective comments and judgements from print finishing plants have been very favourable. When the trials were terminated after 30,000 impressions, the general print quality of all the plates tested was still excellent.

[0056] The lithographic plates bearing a photosensitive layer have been image-wise exposed, developed in an aqueous developer solution, rinsed with water and baked at a temperature between 100°C and 230°C for a time of 40 minutes to 5 minutes. Such treated plates deliver more than 200,000 prints with excellent printing quality. The exposed and developed plates were baked, for example, at a temperature of 230°C for 5 minutes, at a temperature of 150°C for 10 minutes or at a temperature of 120°C for 30 minutes. In each case, the temperature should be equal to or higher than 100°C.

EXAMPLE 2 (according to the invention)

[0057] Lithographic plates were prepared in an identical way as in example 1 but without inserting the plates into a preheated oven. 120,000 prints were obtained with excellent printing quality before the end of the run.

[0058] When said printing plates were not baked at a temperature between 100°C and 230°C for a time of 40 minutes to 5 minutes 100,000 prints were obtained with excellent printing quality before the end of the run.

[0059] When said printing plates were prepared in an identical way as in example 1 but without baking them at a temperature between 100°C and 230°C for a time of 40 minutes to 5 minutes 150,000 prints were obtained with excellent printing quality before the end of the run.

EXAMPLE 3 (comparison)

[0060] A sheet of an aluminum sample as delivered from the supplier, without any further treatment (=as rolled) had been coated with a light sensitive coating (as quoted in EP-A-292801, page 6, lines 31-33) and after image-wise irradiation and development put onto a printing press. In the beginning it gave satisfactory results, but after only 300 impressions the light sensitive coating (the image areas) flaked off and the prints were absolutely unacceptable.

EXAMPLE 4 (according to the invention)

[0061] A sheet of an aluminum sample as delivered from the supplier, without any further treatment (=as rolled) had been coated with a mixture of Alodine NR779 (a composition comprising titanium fluorides, fluoric acid and phosphoric acid and manufactured by Henkel) with an addition of 1 % by weight of polyacrylic acid to a dry thickness of about 100 nm. Thereon was coated a light sensitive coating (as quoted in EP-A-292801, page 6, lines 31-33) and after image-wise irradiation and development the obtained lithographic plate was put onto a printing press. From the beginning it gave satisfactory

results, and the quality of the impressions was good until a length of run of 90000 had been performed.

EXAMPLE 5 (according to the invention)

[0062] A sheet of an aluminum sample as delivered from the supplier, without any further treatment (=as rolled) had been coated with polyacrylic acid to a dry thickness of about 100 nm. Thereon was coated a light sensitive coating (as quoted in EP-A-292801, page 6, lines 31-33) and after image-wise irradiation and development the obtained lithographic plate was put onto a printing press. From the beginning it gave satisfactory results, and the quality of the impressions was good until a length of run of 30000 had been performed.

Claims

1. A lithographic plate support comprising a substrate and a coating thereon derived from an aqueous composition comprising an inorganic sol or metal salt solution and a polycarboxy organic polymeric material wherein the metal salt or the oxide of the inorganic sol within the aqueous composition are capable of cross-linking and making insoluble the polycarboxy organic polymeric material characterized in that the thickness of said coating is at least 30 nm.

2. A lithographic plate support according to claim 1, wherein the inorganic sol is a Type A sol consisting of basic units which are polynuclear ions selected from the group Al(III) Fe(III) Zr(IV) Th(IV) Ce(IV) Ti (IV) forming an inorganic polymer.

3. A lithographic plate support according to claim 1 or 2, wherein the polycarboxy organic polymeric material is selected from the group consisting of polyacrylic acid, polymethacrylic acid, polyethylacrylic acid, polydimethylaminoethylene acrylic acid and co- and terpolymers of the monomeric constituents.

4. A lithographic plate support according to claim 3, wherein the polycarboxy organic polymeric material is polyacrylic acid.

5. A lithographic plate support according to claim 1 or 2, wherein the polycarboxy organic polymeric material is a polymerisate of acrylamidoisobutylene phosphonic acid or a copolymerisate of acrylamidoisobutylene phosphonic acid and acrylic amide.

6. A lithographic support according to claim 2, wherein the Type A sol is selected from the group consisting of zirconia, ceria, titania, hafnia, alumina, iron oxyhydroxide and vanadium sols.

7. A lithographic support as claimed in claim 2, wherein the Type A sol is a zirconia sol and the polycarboxy organic polymeric materials is polyacrylic acid.

8. A lithographic plate support according to claim 7, wherein ZrO_2 of the zirconia sol and polyacrylic acid are present in proportions by weight in the range of 20:1 to 1:20.

9. A lithographic plate support according to any of claims 1 to 8, wherein the substrate is of aluminum.

10. A lithographic plate support according to any of claims 1 to 9, wherein the coating is present at a weight per unit area of 0.02 to 1.0 gm^{-2}.

Patentansprüche

1. Ein Träger einer lithografischen Druckplatte, der ein Substrat und eine darüber vergossene Schicht enthält, die auf Basis einer wäßrigen Zusammensetzung hergestellt ist, die eine anorganische Sol- oder anorganische Metallsalzlösung und ein organisches polymeres Polycarboxymaterial enthält, wobei das Metallsalz oder das Oxid des anorganischen Sols in der wäßrigen Zusammensetzung in der Lage ist, das organische polymere Polycarboxymaterial zu vernetzen und unlöslich zu machen, dadurch gekennzeichnet, daß die Stärke der Schicht wenigstens 30 nm beträgt.

2. Träger einer lithografischen Druckplatte nach Anspruch 1, dadurch gekennzeichnet, daß das anorganische Sol ein Sol des A-Typs ist, dessen Basiseinheiten mehrkernige, ein anorganisches Polymeres bildende Ionen aus der Gruppe bestehend aus Al(III), Fe(III), Zr(IV), Th(IV), Ce(IV) und Ti(IV) sind.

3. Träger einer lithografischen Druckplatte nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das organische polymere Polycarboxymaterial Polyacrylsäure, Polymethacrylsäure, Polyethylacrylsäure, Polydimethylaminoethylenacrylsäure oder ein Copolymeres oder Terpolymeres der monomeren Komponenten ist.

4. Träger einer lithografischen Druckplatte nach Anspruch 3, dadurch gekennzeichnet, daß das organische polymere Polycarboxymaterial Polyacrylsäure ist.

5. Träger einer lithografischen Druckplatte nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das organische polymere Polycarboxymaterial ein Polymerisat von Acrylamidoisobutylen-phosphonsäure oder ein Copolymerisat von Acrylamidoisobutylenphosphonsäure und Acrylamid ist.

6. Träger einer lithografischen Druckplatte nach Anspruch 2, dadurch gekennzeichnet, daß das Sol des A-Typs ein Zirconoxidsol, Ceriumoxidsol, Titandioxidsol, Hafniumoxidsol, Tonerdesol, Eisenoxyhydroxidsol oder Vanadiumoxidsol ist.

7. Träger einer lithografischen Druckplatte nach Anspruch 2, dadurch gekennzeichnet, daß das Sol des A-Typs ein Zirconoxidsol und das organische polymere Polycarboxymaterial Polyacrylsäure ist.

8. Träger einer lithografischen Druckplatte nach Anspruch 7, dadurch gekennzeichnet, daß ZrO_2 des Zirconoxidsols und Polyacrylsäure in einem Gewichtsverhältnis zwischen 20:1 und 1:20 enthalten sind.

9. Träger einer lithografischen Druckplatte nach irgendeinem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß das Substrat ein Aluminiumsubstrat ist.

10. Träger einer lithografischen Druckplatte nach irgendeinem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die Schicht in einem Gewicht pro Flächeneinheit zwischen 0,02 und 1,0 gm-2 enthalten ist.

Revendications

1. Support de cliché lithographique comprenant un substrat et un revêtement sur ce dernier dérivé d'une composition aqueuse comprenant un sol inorganique ou une solution de sel métallique et une matière polymère organique polycarboxylée, dans lequel le sel métallique ou l'oxyde du sol inorganique dans la composition aqueuse sont capables de réticuler et de rendre insoluble la matière polymère organique polycarboxylée, caractérisé en ce que l'épaisseur dudit revêtement s'élève à au moins 30 nm.

2. Support de cliché lithographique selon la revendication 1, dans lequel le sol inorganique est un sol de type A constitué par des unités basiques qui représentent des ions polynucléaires choisis parmi le groupe comprenant Al(III) Fe(III) Zr(IV) Th(IV) Ce (IV) Ti(IV) formant un polymère inorganique.

3. Support de cliché lithographique selon la revendication 1 ou 2, dans lequel la matière polymère organique polycarboxylée est choisie parmi le groupe constitué par l'acide polyacrylique, l'acide polyméthacrylique, l'acide polyéthylacrylique, l'acide polydiméthylaminoéthylèneacrylique, ainsi que par des copolymères et des terpolymères des constituants monomères.

4. Support de cliché lithographique selon la revendication 3, dans lequel la matière polymère organique polycarboxylée est l'acide polyacrylique.

5. Support de cliché lithographique selon la revendication 1 ou 2, dans lequel la matière polymère organique polycarboxylée est un polymère d'acide acrylamidoisobutylène-phosphonique ou un copolymère d'acide acrylamidoisobutylène-phosphonique et d'amide acrylique.

6. Support lithographique selon la revendication 2, dans lequel le sol de type A est choisi parmi le groupe constitué par des sols d'oxyde de zirconium, d'oxyde de cérium, d'oxyde de titane, d'oxyde de hafnium, d'oxyde d'alumine, d'oxyhydroxyde de fer et de vanadium.

7. Support lithographique selon la revendication 2, dans lequel le sol de type A est un sol d'oxyde de zirconium et la matière polymère organique polyhydroxylée est l'acide polyacrylique.

8. Support de cliché lithographique selon la revendication 7, dans lequel le ZrO_2 du sol d'oxyde de zirconium et l'acide polyacrylique sont présents dans des proportions en poids dans le domaine de 20:1 à 1:20.

9. Support de cliché lithographique selon l'une quelconque des revendications 1 à 8, dans lequel le substrat est un substrat en aluminium.

10. Support de cliché lithographique selon l'une quelconque des revendications 1 à 9, dans lequel le poids du revêtement par unité de surface s'élève de 0,02 à 1,0 g^{-2}.