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(54) Method of making a negative-working lithographic printing plate.

(57) A method for preparing a negative-working lithographic printing plate is provided which comprises the steps of (i) providing a lithographic printing plate precursor comprising (a) a grained and anodized aluminum support which has been subjected to a post-anodic treatment with a hydrophilising agent which is a polymer containing acrylic acid monomeric units, and (b) on said support a coating comprising hydrophobic thermoplastic polymer particles and an infrared light absorbing agent, (ii) exposing said coating to heat, thereby inducing coalescence of said thermoplastic polymer particles at exposed areas of said coating, and (iii) developing said precursor by applying a gum solution to said coating, thereby removing non-exposed areas of said coating from said support.

According to the above method the printing plates exhibit an improved stability of the clean-out and the background stain after ageing.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for making a lithographic printing plate precursor and to a method for making a lithographic printing plate.

BACKGROUND OF THE INVENTION

[0002] In lithographic printing, a so-called printing master such as a printing plate is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a printed copy is obtained by applying ink to said image and then transferring the ink from the master onto a receiver material, which is typically paper. In conventional, so-called "wet" lithographic printing, ink as well as an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-accepting, ink-repelling) areas. In so-called "driographic" printing, the lithographic image consists of ink-accepting and ink-abhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

[0003] Printing masters are generally obtained by the so-called computer-to-film (CtF) method wherein various pre-press steps such as typeface selection, scanning, color separation, screening, trapping, layout and imposition are accomplished digitally and each color selection is transferred to graphic arts film using an imagesetter. After processing, the film can be used as a mask for the exposure of an imaging material called plate precursor and after plate processing, a printing plate is obtained which can be used as a master. Since about 1995, the so-called 'computer-to-plate' (CtP) method has gained a lot of interest. This method, also called 'direct-to-plate', bypasses the creation of film because the digital document is transferred directly to a plate precursor by means of a so-called plate-setter.

[0004] Especially thermal plates, which are sensitive to heat or infrared light, are widely used in computer-to-plate methods because of their daylight stability. Such thermal materials may be exposed directly to heat, e.g. by means of a thermal head, but preferably comprise a compound that converts absorbed light into heat and are therefore suitable for exposure by lasers, especially infrared laser diodes. The heat, which is generated on image-wise exposure, triggers a (physico-)chemical process, such as ablation, polymerization, insolubilization by cross-linking of a polymer, decomposition, or particle coagulation of a thermoplastic polymer latex, and after optional processing, a lithographic image is obtained. Many thermal plate materials are based on heat-induced ablation. A problem associated with ablative plates is the generation of debris which is difficult to remove and may disturb the printing process or may contaminate the exposure optics of the plate-setter. As a result, such ablative plates require a processing step for removing the debris from the exposed material.

[0005] The support of a lithographic printing plate is typically an electrochemically grained and anodized aluminum plate. The anodized aluminum support may be subject to a so-called post-anodic treatment to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with a sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulfonic acid, polyvinylbenzenesulfonic acid, sulfuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulfonated aliphatic aldehyde.

[0006] EP 770 497 discloses a method wherein an imaging material comprising an image-recording layer of a hydrophilic binder, a compound capable of converting light to heat and hydrophobic thermoplastic polymer particles, is image-wise exposed, thereby inducing coalescence of the polymer particles and converting the image-recording layer into an hydrophobic phase which defines the printing areas of the printing master. Subsequently the image-wise exposed precursor is developed by rinsing it with plain water or an aqueous liquid.

[0007] EP 1 342 568 discloses a method wherein an imaging material comprising an image-recording layer of a hydrophilic binder, a compound capable of converting light to heat and hydrophobic thermoplastic polymer particles, is image-wise exposed, thereby inducing coalescence of the polymer particles and converting the image-recording layer into an hydrophobic phase which defines the printing areas of the printing master. Subsequently the image-wise exposed precursor is processed with a gum solution, thereby developing and gumming the plate in a single step.
In this single step process, the image-recording layer at the non-exposed areas is removed with the gum solution from the support, revealing the hydrophilic surface of the support, also called "clean-out", and simultaneously the hydrophilic surface in these non-image areas is protected from contamination (fingerprints, fats, oils, dust, oxidation, etc.) by the gum.

[0008] An important prerequisite for a high quality printing plate precursor is its shelf-life stability. A problem associated with printing plate precursors of the prior art which are based on heat-induced coagulation of thermoplastic polymer particles and are processed with a gum solution, is a lack in shelf-life stability: after ageing the precursor under high humidity condition the "clean-out" is insufficient and toning appears. "Toning" means an increased tendency of ink-acceptance at the non-image areas. It is important in the preparation of high quality printing plates to avoid toning as much as possible.

SUMMARY OF THE INVENTION

[0009] It is an object of the present invention to provide a method for making a negative-working lithographic printing plate with an improved clean-out and with an improved shelf-life stability of the cleaning-out capability.

[0010] It is also an object of the present invention to provide a method for making a negative-working lithographic printing plate with an improved clean-out, an improved shelf-life stability of the cleaning-out capability and a high printing run length.

[0011] According to the present invention, these objects are realized by the method of preparing a negative-working lithographic printing plate comprising the steps of (1) providing a lithographic printing plate precursor comprising (i) a grained and anodized aluminum support which has been subjected to a post-anodic treatment with a hydrophilising agent which is a polymer containing acrylic acid monomeric units, and (ii) on said support a coating comprising hydrophobic thermoplastic polymer particles and an infrared light absorbing agent, (2) exposing said coating to heat, thereby inducing coalescence of said thermoplastic polymer particles at exposed areas of said coating, and (3) developing said precursor by applying a gum solution to said coating, thereby removing non-exposed areas of said coating from said support.

[0012] According to another embodiment of the present invention, a negative-working lithographic printing plate precursor is prepared comprising the steps of (1) providing a grained and anodised aluminum support, (2) treating the support with a hydrophilising agent which is a polymer containing acrylic acid monomeric units, and (3) applying on said support a coating comprising hydrophobic thermoplastic polymer particles and an infrared light absorbing agent.

[0013] In the present invention, it has been found that treatment of the grained and anodized aluminum support with a polymer containing acrylic acid monomeric units improves the clean-out in the developing step of the image-wise exposed precursor with a gum solution and delivers a toning free printing plate, even after storing the printing plate precursor under high humidity conditions. The method for measuring the clean-out is described in the examples.

[0014] Specific embodiments of the present invention are defined in the dependent claims. Further advantages and embodiments of the present invention will become apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The support of the plate precursor and of the printing plate is a grained and anodised aluminum support. Graining an anodizing of aluminum supports is well known. The grained aluminum support used in the material of the present invention is preferably an electrochemically grained support. The acid used for graining can be e.g. nitric acid or sulphuric acid. The acid used for graining preferably comprises hydrogen chloride. Also mixtures of e.g. hydrogen chloride and acetic acid can be used. The relation between electrochemical graining and anodizing parameters such as electrode voltage, nature and concentration of the acid electrolyte or power consumption on the one hand and the obtained lithographic quality in terms of Ra and anodic weight (g/m^2 of Al_2O_3 formed on the aluminum surface) on the other hand is well known. More details about the relation between various production parameters and Ra or anodic weight can be found in e.g. the article "Management of Change in the Aluminium Printing Industry" by F. R. Mayers, published in the ATB Metallurgie Journal, volume 42 nr. 1-2 (2002) pag. 69.

[0016] The grained and anodized aluminum support is further treated with a compound comprising a hydrophilising agent. In this post-anodic treatment the grained and anodized aluminum support is brought into contact with a solution of the hydrophilising agent. Typically, in prior art materials, a post-anodic treatment was carried out with a solution of polyvinylphosphonic acid or a salt of zirconium such as sodium hexafluorozirconate or zirconium fluoride.

[0017] A further improvement of the shelf-life stability of the clean-out is obtained with an increasing amount of acrylic acid monomeric units in the hydrophilising polymer. In accordance with the present invention, the amount of acrylic acid monomeric units in the hydrophilising polymer is preferably at least 30 mol%, more preferably at least 50 mol%, most preferred at least 75 mol%. The best results are obtained with a hydrophilising polymer consisting essentially of acrylic acid monomeric units.

[0018] Examples of polymers containing acrylic acid monomeric units which can be used as hydrophilising agent in the post-anodic treatment are

POL-01 = GLASCOL E15, a polyacrylic acid, commercially available from ALLIED COLLOIDS

POL-02 = a copolymer of acrylic acid and vinylphosphonic acid (mol ratio 1.1:1)

[0019] In the post-anodic treatment an aqueous solution of the polymer comprising acrylic acid monomeric units is brought into contact with the grained and anodized aluminum support. An aqueous solution of the polymer is defined herein as a solution of the polymer in water or in a mixture of at least 50% (vol/vol) of water and a water-miscible organic solvent such as an alcohol e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones e.g. 2-propanone and 2-butanone etc.

[0020] The concentration of the polymer in the aqueous solution is preferably in the range between 0.01 wt.% and 10.0 wt.%, more preferably between 0.05% (w/w) and 5 wt.%, most preferably 0.05 wt.% and 1.5 wt.%. The pH of the polymer solution ranges preferably between 1 and 6, more preferably between 3 and 5.5. The temperature of the polymer solution in this treatment ranges preferably between 10°C and 90°C, more preferably between 30°C and 60°C, most preferably between 35°C and 50°C. The dwell-time, defined as the time of contact between the polymer solution and the plate, ranges preferably between 0.1 second and 5 minutes, more preferably between 0.5 seconds and 2 minutes, most preferably between 1 second and 1 minute. The technique to bring the polymer solution into contact with the plate is preferably selected from dip coating, spray coating, slot coating, reverse roll coating, electrochemical coating or by immersion; spray coating and dip coating are more preferred. Single pass processes are also preferred since they facilitate the avoidance of contamination which could otherwise occur as a consequence of circulation of the solution.

[0021] The grained and anodised aluminum support, treated with a polymer containing acrylic acid monomeric units, may be a sheet-like material such as a plate or it may be a cylindrical element such as a sleeve which can be slid around a print cylinder of a printing press.

[0022] The coating provided on the support comprises an image-recording layer which contains hydrophobic thermoplastic polymer particles. Specific examples of suitable hydrophobic polymers are e.g. polyethylene, poly(vinyl chloride), poly(methyl (meth)acrylate), poly(ethyl (meth)acrylate), poly(vinylidene chloride), poly(meth)acrylonitrile, poly(vinyl carbazole), polystyrene or copolymers thereof. Polystyrene and poly(meth)acrylonitrile or their derivatives are highly preferred embodiments. According to such preferred embodiments, the thermoplastic polymer comprises at least 50 wt.% of polystyrene, and more preferably at least 60 wt.% of polystyrene. In order to obtain sufficient resistivity towards organic chemicals, such as the hydrocarbons used in plate cleaners, the thermoplastic polymer preferably comprises at least 5 wt.%, more preferably at least 30 wt.% of nitrogen containing monomeric units or of units which correspond to monomers that are characterized by a solubility parameter larger than 20, such as (meth)acrylonitrile. Suitable examples of such nitrogen containing monomeric units are disclosed in EP-A 1 219 416.

[0023] According to the most preferred embodiment, the thermoplastic polymer is a copolymer consisting of styrene and acrylonitrile units in a weight ratio between 1:1 and 5:1 (styrene:acrylonitrile), e.g. in a 2:1 ratio.

[0024] The weight average molecular weight of the thermoplastic polymer particles may range from 5,000 to 1,000,000 g/mol. The hydrophobic particles preferably have a number average particle diameter below 200 nm, more preferably between 5 nm and 150 nm, most preferably between 10 nm and 100 nm. The amount of hydrophobic thermoplastic polymer particles contained in the image-recording layer is preferably between 20 wt.% and 95 wt.% and more preferably between 25 wt.% and 90 wt.% and most preferably between 30 wt.% and 85 wt.%.

[0025] The hydrophobic thermoplastic polymer particles are present as a dispersion in an aqueous coating liquid of the image-recording layer and may be prepared by the methods disclosed in US 3,476,937. Another method especially suitable for preparing an aqueous dispersion of the thermoplastic polymer particles comprises:

- dissolving the hydrophobic thermoplastic polymer in an organic water immiscible solvent,
- dispersing the thus obtained solution in water or in an aqueous medium and
- removing the organic solvent by evaporation.

[0026] The image-recording layer preferably comprises a hydrophilic binder, e.g. homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co) polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

[0027] In accordance with the present invention the image-recording layer comprises an infrared absorbing agent. The infrared absorbing agents are compounds capable of converting infrared light into heat. Particularly useful infrared absorbing agents capable of converting infrared light into heat are for example infrared dyes, carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides, and conductive polymer dispersions such as polypyrrole, polyaniline or polythiophene dispersions.

[0028] The image-recording layer may also contain other ingredients such as additional binders, surfactants, colorants and development inhibitors or accelerators. The colorants are preferably dyes or pigments which provide a visible image after processing.

[0029] The coating may also contain one or more additional layer(s), adjacent to the image-recording layer. Such additional layer can e.g. be an adhesion-improving layer between the image-recording layer and the support; or a light-absorbing layer comprising one or more of the above compounds that are capable of converting infrared light into heat; or a covering layer which is removed during processing with the gum solution.

[0030] A gum solution is typically an aqueous liquid which comprises one or more surface protective compounds that are capable of protecting the lithographic image of a printing plate against contamination, e.g. by oxidation, fingerprints, fats, oils or dust, or damaging, e.g. by scratches during handling of the plate. Suitable examples of such compounds are film-forming hydrophilic polymers or surfactants. The layer that remains on the plate after treatment with the gum solution preferably comprises between 0.1 and 20 g/m^2 of the surface protective compound.

[0031] A gum solution is normally supplied as a concentrated solution which is diluted by the end user with water before use. In the present description, all concentrations of compounds present in the gum solution are expressed as percentage by weight (wt.% or % w/w) relative to the non-diluted gum solution, unless otherwise indicated.

[0032] Preferred polymers for use as protective compound in the gum solution are gum arabic, pullulan, cellulose derivatives such as carboxymethylcellulose, carboxyethylcellulose or methylcellulose, (cyclo)dextrin, poly(vinyl alcohol), poly(vinyl pyrrolidone), polysaccharide, homo- and copolymers of acrylic acid, methacrylic acid or acrylamide, a copolymer of vinyl methyl ether and maleic anhydride, a copolymer of vinyl acetate and maleic anhydride or a copolymer of styrene and maleic anhydride. Highly preferred polymers are homo- or copolymers of monomers containing carboxylic, sulfonic or phosphonic groups or the salts thereof, e.g. (meth)acrylic acid, vinyl acetate, styrene sulfonic acid, vinyl sulfonic acid, vinyl phosphonic acid or acrylamidopropane sulfonic acid.

[0033] Examples of surfactants for use as surface protective agent include anionic or nonionic surfactants. The gum solution may also comprise one or more of the above hydrophilic polymers as surface protective agent and, in addition, one or more surfactants to improve the surface properties of the coated layer. The surface tension of the gum solution is preferably from 40 to 50 mN/m.

[0034] The gum solution comprises preferably an anionic surfactant, more preferably an anionic surfactant whereof the anionic group is a sulphonic acid group.

[0035] Examples of the anionic surfactant include aliphates, abietates, hydroxyalkanesulfonates, alkanesulfonates, dialkylsulfosuccinates, straight-chain alkylbenzenesulfonates, branched alkylbenzenesulfonates, alkylnaphthalenesulfonates, alkylphenoxypolyoxyethylenepropylsulfonates, salts of polyoxyethylene alkylsulfophenyl ethers, sodium N-methyl-N-oleyltaurates, monoamide disodium N-alkylsulfosuccinates, petroleum sulfonates, sulfated castor oil, sulfated tallow oil, salts of sulfuric esters of aliphatic alkylesters, salts of alkylsulfuric esters, sulfuric esters of polyoxyethylene-alkylethers, salts of sulfuric esters of aliphatic monoglycerides, salts of sulfuric esters of polyoxyethylenealkylphenylethers, salts of sulfuric esters of polyoxyethylenestyrylphenylethers, salts of alkylphosphoric esters, salts of phosphoric esters of polyox-yethylenealkylethers, salts of phosphoric esters of polyoxyethylenealkylphenylethers, partially saponified compounds of styrenemaleic anhydride copolymers, partially saponified compounds of olefin-maleic anhydride copolymers, and naphthalenesulfonateformalin condensates. Particularly preferred among these anionic surfactants are dialkylsulfosuccinates, salts of alkylsulfuric esters and alkylnaphthalenesulfonates.

[0036] Specific examples of suitable anionic surfactants include sodium dodecylphenoxybenzene disulfonate, the sodium salt of alkylated naphthalenesulfonate, disodium methylene-dinaphtalene-disulfonate, sodium dodecyl-benzenesulfonate, sulfonated alkyl-diphenyloxide, ammonium or potassium perfluoroalkylsulfonate and sodium dioctyl-sulfosuccinate.

[0037] Suitable examples of the nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene polystyryl phenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene polyoxypropylene block polymers, partial esters of glycerinaliphatic acids, partial esters of sorbitanaliphatic acid, partial esters of pentaerythritolaliphatic acid, propyleneglycolmonoaliphatic esters, partial esters of sucrosealiphatic acids, partial esters of polyoxyethylenesorbitanaliphatic acid, partial esters of polyoxyethylenesorbitolaliphatic acids, polyethyleneglycolaliphatic esters, partial esters of poly-glycerinaliphatic acids, polyoxyethylenated castor oils, partial esters of polyoxyethyleneglycerinaliphatic acids, aliphatic diethanolamides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamines, triethanolaminealiphatic esters, and trialkylamine oxides. Particularly preferred among these nonionic surfactants are polyoxyethylene alkylphenyl ethers and poloxyethylene-polyoxypropylene block polymers. Further, fluorinic and siliconic anionic and nonionic surfactants may be similarly used.

[0038] Two or more of the above surfactants may be used in combination. For example, a combination of two or more different anionic surfactants or a combination of an anionic surfactant and a nonionic surfactant may be preferred. The amount of such a surfactant is not specifically limited but is preferably from 0.01 to 20 wt.%.

[0039] A typical gum solution has a pH from 3 to 8. The pH of the gum solution is usually adjusted with a mineral acid, an organic acid or an inorganic salt in an amount of from 0.01 to 2 wt.%. Examples of the mineral acids include nitric acid, sulfuric acid, phosphoric acid and metaphosphoric acid. Especially organic acids are used as pH control agents and as desensitizing agents. Examples of the organic acids include carboxylic acids, sulfonic acids, phosphonic acids or salts thereof, e.g. succinates, phosphates, phosphonates, sulfates and sulfonates. Specific examples of the organic acid include citric acid, acetic acid, oxalic acid, malonic acid, p-toluenesulfonic acid, tartaric acid, malic acid, lactic acid, levulinic acid, phytic acid and organic phosphonic acid.

[0040] In a non-limiting explanation it may be understood that, due to the low pH-value of the gum solution, a completely removal of the coating is not easily obtained in the processing step with a gum solution. Therefor it has been found that specially due to the post-anodic treatment with a (co)polymer containing acrylic acid monomeric units as hydrophilising agent surprisingly the clean-out is improved specifically after high humidity shelf-life ageing of the precursor and toning is avoided. According to another embodiment of the present invention, the gum solution further comprises preferably an inorganic salt, more preferably a mono or dibasic phosphate salt, most preferably an alkali-metal dihydrogen phosphate such as KH_2PO_4 or NaH_2PO_4. It has also been found that the cleaning-out capability after shelf-life ageing is further improved when an inorganic salt is added to the gum solution, such as an inorganic phosphate.

[0041] Examples of the inorganic salt include magnesium nitrate, monobasic sodium phosphate, dibasic sodium phosphate, nickel sulfate, sodium hexametaphosphate and sodium tripolyphosphate. Other inorganic salts can be used as corrosion inhibiting agents, e.g. magnesium sulfate or zinc nitrate. The mineral acid, organic acid or inorganic salt may be used singly or in combination with one or more thereof.

[0042] In accordance with another embodiment of the present invention, the gum solution as developer in the processing of the plate comprises preferably a mixture of an anionic surfactant and an inorganic salt. In this mixture the anionic surfactant is preferably an anionic surfactant with a sulphonic acid group, more preferably an alkali-metal salt of a mono- or di-alkyl substituted diphenylether-sulphonic acid, and the inorganic salt is preferably a mono or dibasic phosphate salt, more preferably an alkali-metal dihydrogen phosphate, most preferably KH_2PO_4 or NaH_2PO_4.

[0043] In accordance with another embodiment of the present invention, the gum solution comprising a mixture of an anionic surfactant and an inorganic salt has preferably a pH-value between 6 and 8, more preferably between 6.2 and 7.5.

[0044] Besides the foregoing components, a wetting agent such as ethylene glycol, propylene glycol, triethylene glycol, butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, glycerin, trimethylol propane and diglycerin may also be present in the gum solution. The wetting agent may be used singly or in combination with one or more thereof. In general, the foregoing wetting agent is preferably used in an amount of from 1 to 25 wt.%.

[0045] Further, a chelate compound may be present in the gum solution. Calcium ion and other impurities contained in the diluting water can have adverse effects on printing and thus cause the contamination of printed matter. This problem can be eliminated by adding a chelate compound to the diluting water. Preferred examples of such a chelate compound include organic phosphonic acids or phosphonoalkanetricarboxylic acids. Specific examples are potassium or sodium salts of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, 1-hydroxyethane-1,1-diphosphonic acid and aminotri(methylenephosphonic acid). Besides these sodium or potassium salts of these chelating agents, organic amine salts are useful. The preferred amount of such a chelating agent to be added is from 0.001 to 1.0 wt.% relative to the gum solution in diluted form.

[0046] Further, an antiseptic and an anti-foaming agent may be present in the gum solution. Examples of such an antiseptic include phenol, derivatives thereof, formalin, imidazole derivatives, sodium dehydroacetate, 4-isothiazoline-3-one derivatives, benzoisothiazoline-3-one, benztriazole derivatives, amidineguanidine derivatives, quaternary ammonium salts, pyridine derivatives, quinoline derivatives, guanidine derivatives, diazine, triazole derivatives, oxazole and oxazine derivatives. The preferred amount of such an antiseptic to be added is such that it can exert a stable effect on bacteria, fungi, yeast or the like. Though depending on the kind of bacteria, fungi and yeast, it is preferably from 0.01 to 4 wt.% relative to the gum solution in diluted form. Further, preferably, two or more antiseptics may be used in combination to exert an aseptic effect on various fungi and bacteria. The anti-foaming agent is preferably silicone anti-foaming agents. Among these anti-foaming agents, either an emulsion dispersion type or solubilized type anti-foaming agent may be used. The proper amount of such an anti-foaming agent to be added is from 0.001 to 1.0 wt.% relative to the gum solution in diluted form.

[0047] Besides the foregoing components, an ink receptivity agent may be present in the gum solution if desired. Examples of such an ink receptivity agent include turpentine oil, xylene, toluene, low heptane, solvent naphtha, kerosine, mineral spirit, hydrocarbons such as petroleum fraction having a boiling point of about 120°C to about 250°C, diester phthalates (e.g., dibutyl phthalate, diheptyl phthalate, di-n-octyl phthalate, di(2-ethylhexyl) phthalate, dinonyl phthalate, didecyl phthalate, dilauryl phthalate, butylbenzyl phthalate), aliphatic dibasic esters (e.g., dioctyl adipate, butylglycol adipate, dioctyl azelate, dibutyl sebacate, di(2-ethylhexyl) sebacate dioctyl sebacate), epoxidated triglycerides (e.g., epoxy soyabean oil), ester phosphates (e.g., tricresyl phosphate, trioctyl phosphate, trischloroethyl phosphate) and plasticizers having a solidification point of 15°C or less and a boiling point of 300°C or more at one atmospheric pressure such as esters of benzoates (e.g., benzyl benzoate). Examples of other solvents which can be used in combination with these solvents include ketones (e.g., cyclohexanone), halogenated hydrocarbons (e.g., ethylene dichloride), ethylene glycol ethers (e.g., ethylene glycol monomethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobutyl ether), aliphatic acids (e.g., caproic acid, enathic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, heptadecylic acid, stearic acid, nonadecanic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, heptacosanoic acid, montanic acid, melissic acid, lacceric acid, isovaleric acid) and unsaturated aliphatic acids (e.g., acrylic acid, crotonic acid, isocrotonic acid, undecyclic acid, oleic acid, elaidic acid, cetoleic acid, erucic acid, butecidic acid, sorbic acid, linoleic acid, linolenic acid, arachidonic acid, propiolic acid, stearolic acid, clupanodonic acid, tariric acid, licanic acid). Preferably, it is an aliphatic acid which is liquid at a temperature of 50°C, more preferably has from 5 to 25 carbon atoms, most preferably has from 8 to 21 carbon atoms. The ink receptivity agent may be used singly or in combination with one or more thereof. The ink receptivity agent is preferably used in an amount of from 0.01 to 10 wt.%, more preferably from 0.05 to 5 wt.%. The foregoing ink receptivity agent may be present as an oil-in-water emulsion or may be solubilized with the aid of a solubilizing agent.

[0048] The viscosity of the gum solution can be adjusted to a value of e.g. between 1.7 and 5 cP, by adding viscosity increasing compounds, such as poly(ethylene oxide), e.g. having a molecular weight between 10^5 and 10^7. Such compounds can be present in a concentration of 0.01 to 10 g/l.

[0049] A baking gum has a similar composition as described above, with the additional preference towards compounds that do not evaporate at the usual bake temperatures. Specific examples of suitable baking gum solutions are described in e.g. EP-A 222 297, EP-A 1 025 992, DE-A 2 626 473 and US 4,786,581.

[0050] The printing plate precursors used in the present invention are exposed to heat or to infrared light, e.g. by means of an infrared laser or LEDs. Preferably, a laser emitting near infrared light having a wavelength in the range from about 700 to about 1500 nm is used, e.g. a semiconductor laser diode, a Nd:YAG or a Nd:YLF laser. The required laser power depends on the sensitivity of the image-recording layer, the pixel dwell time of the laser beam, which is determined by the spot diameter (typical value of modern plate-setters at $1/e^2$ of maximum intensity : 10-25 μm), the scan speed and the resolution of the exposure apparatus (i.e. the number of addressable pixels per unit of linear distance, often expressed in dots per inch or dpi; typical value : 1000-4000 dpi). Two types of laser-exposure apparatuses are commonly used : internal (ITD) and external drum (XTD) plate-setters. ITD plate-setters for thermal plates are typically characterized by a very high scan speed up to 500 m/sec and may require a laser power of several Watts. XTD plate-setters for thermal plates having a typical laser power from about 200 mW to about 1 W operate at a lower scan speed, e.g. from 0.1 to 10 m/sec.

[0051] Due to the heat generated during the exposure step, the hydrophobic thermoplastic polymer particles fuse or coagulate so as to form a hydrophobic phase which corresponds to the printing areas of the printing plate. Coagulation may result from heat-induced coalescence, softening or melting of the thermoplastic polymer particles. There is no specific upper limit to the coagulation temperature of the thermoplastic hydrophobic polymer particles, however the temperature should be sufficiently below the decomposition temperature of the polymer particles. Preferably the coagulation temperature is at least 10°C below the temperature at which the decomposition of the polymer particles occurs. The coagulation temperature is preferably higher than 50°C, more preferably above 100°C.

[0052] In the development step, the non-exposed areas of the image-recording layer are removed by supplying a gum or baking gum solution without essentially removing the exposed areas, i.e. without affecting the exposed areas to an extent that renders the ink-acceptance of the exposed areas inacceptable. The development by supplying a gum or baking gum may be combined with mechanical rubbing, e.g. by a rotating brush. The gum or baking gum solution can be applied to the plate e.g. by rubbing in with an impregnated pad, by dipping, (spin-)coating, spraying, pouring-on, either by hand or in an automatic processing apparatus. After applying the baking gum solution, the plate can be dried before baking or is dried during the baking process itself. The baking process can proceed at a temperature above the coagulation temperature of the thermoplastic polymer particles, e.g. between 100°C and 230°C for a period of 5 to 40 minutes. For example the exposed and developed plates can be baked 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. Baking can be done in conventional hot air ovens or by irradiation with lamps emitting in the infrared or ultraviolet spectrum.

EXAMPLES

INVENTION EXAMPLES 1 TO 7 AND COMPARATIVE EXAMPLES 1 TO 5

Preparation of lithographic support S-01

[0053] A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 10 g/l of sodium hydroxide at 39°C for 35 seconds and rinsed with demineralized water for 30 seconds. The foil was then electrochemically grained during 30 seconds using an alternating current at a current density of 1000 A/m^2 in a mixed acid aqueous solution containing 8.1 g/l of hydrochloric acid and 21.7 g/l of acetic acid at a temperature of 30°C. After rinsing with demineralized water for 30 seconds, the aluminum foil was then desmutted by etching with an aqueous solution containing 128 g/l of phosphoric acid at 43°C for 35 seconds and rinsing with demineralized water for 30 seconds. Subsequently, the foil was subjected to an anodic oxidation during 30 seconds in an aqueous solution containing 154 g/l of sulfuric acid at a 50°C, using a DC voltage at a current density of 2050 A/m^2, and rinsed with demineralized water for 30 seconds. The foil has an anodic oxidation layer thickness of 4.2 g/m^2, measured by gravimetric experiments. The foil has a surface topography with an average center-line roughness Ra of 0.21 µm, measured with a TALYSURF 10 apparatus from TAYLOR HOBSON Ltd.

Preparation of lithographic support S-02

[0054] The same procedure as above was followed with the proviso that the current density during graining and anodizing was 1130 A/m^2 and 1200 A/m^2 respectively. The support S-02 has an anodic oxidation film of 4.5 g/m^2 and a surface topography with an average center-line roughness Ra of 0.24 µm, measured with a TALYSURF 10 apparatus from TAYLOR HOBSON Ltd.

Post-anodic treatment (PAT)

[0055] The grained and anodized aluminum support S-01 and S-02 were then treated by passing the web through a tank, containing a post-anodic treatment solution as defined in Table 1. For the post-anodic treatment of support S-01 the temperature of the treatment was 42°C and the dipping time was 30 seconds. For the post-anodic treatment of support S-02 the temperature of the treatment was 45°C and the dipping time was 30 seconds. The compound for the post-anodic treatment and the concentration of the compound in water are indicated in Table 1.

Table 1:

POST-ANODIC TREATMENT (PAT-number)	SUPPORT (type)	COMPOUND for POST-ANODIC TREATMENT (PAT-compound)	CONCENTRATION of PAT-compound in water (g/l)
PAT-01	S-01	POL-01	1.2
PAT-02	S-01	POL-01	2.0
PAT-03	S-01	POL-01	5.8
PAT-04	S-01	POL-02	1.51
PAT-05	S-01	POL-02	2.8
PAT-06	S-01	Polyvinylphosphonic acid	2.3
PAT-07	S-01	Polyvinylphosphonic acid	6
PAT-08	S-02	K_2ZrF_6	2.8
PAT-09	S-02	K_2ZrF_6	5
PAT-10	S-02	K_2ZrF_6	10.2

Preparation of printing plate precursor

[0056] The printing plate precursors were produced by coating the solution defined in Table 2 onto the different post-anodic treated lithographic substrates as indicated in Table 1. The coating solution was applied at a wet coating thickness of about 30 µm and then dried at 60°C. The dry coating weight for each example was measured gravimetrically and ranges between 0.71 and 0.85 g/m^2 as indicated in Table 3.

Table 2: composition of the coating solution

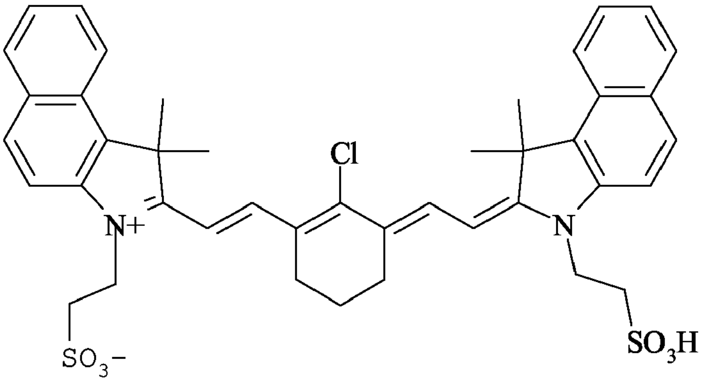
INGREDIENTS	Parts (grams)
Latex-dispersion (1)	114.1
Demineralized water	352.9
1 % (w/w) solution of IR-dye-1 in demineralized water (2)	300
1.5 % (w/w) solution of GLASCOL E15 in demineralized water (3)	200
7.5 % (w/w) solution of Dye-1 in deminerilized water (4)	28

Table continued

INGREDIENTS	Parts (grams)
0.0001 % (w/w) solution of Surfactant-1 in demineralized water (5)	5

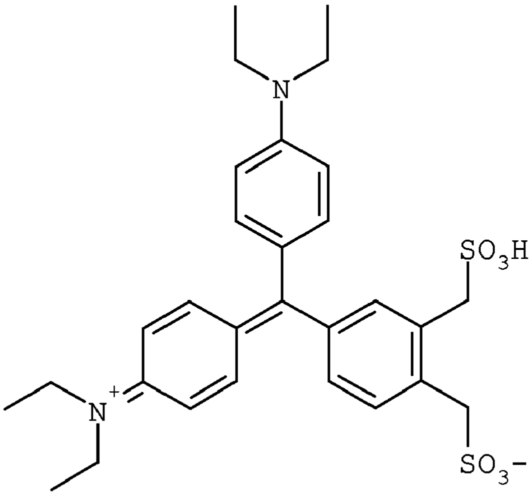
(1) Latex-dispersion of a copolymer of styrene and acrylonitrile (mol-ratio 1:1) in a concentration of 19.2 % (w/w) in demineralized water, having a particle size ranging between 60 and 70 nm and stabilized by an anionic wetting agent.

(2) The infrared absorbing dye, IR-dye-1, has the following chemical structure:



(3) GLASCOL E15 is a polyacrylic acid, commercially available of ALLIED COLLOIDS MANUFACTURING Co. Ltd..

(4) The contrast dye, Dye-1, has the following chemical structure:



(5) Surfactant-1 is FT248, a fluoro-surfactant commercially available from BAYER.

Table 3:

PRECURSOR (number)	SUPPORT (type)	POST-ANODIC TREATMENT (PAT-number)	COATING THICKNESS (g/m^2)
PRE-01	S-01	PAT-01	0.77
PRE-02	S-01	PAT-02	0.73
PRE-03	S-01	PAT-03	0.71

Table continued

PRECURSOR (number)	SUPPORT (type)	POST-ANODIC TREATMENT (PAT-number)	COATING THICKNESS (g/m^2)
PRE-04	S-01	PAT-04	0.72
PRE-05	S-01	PAT-05	0.66
PRE-06	S-01	PAT-06	0.72
PRE-07	S-01	PAT-07	0.68
PRE-08	S-02	PAT-08	0.82
PRE-09	S-02	PAT-09	0.83
PRE-10	S-02	PAT-10	0.77

Ageing

[0057] The printing plate precursors of the Invention Examples 1 to 5 and of the Comparative Examples 1 to 5, as indicated in Table 4, were aged by storing the precursors, packed in a black non-humidity proof paper without interleaving, during 7 days at 35°C and 80% relative humidity.

Exposure

[0058] After ageing, the printing plate precursors were exposed with a CREO TRENDSETTER 3244 T, a plate-setter available from CREO, Burnaby, Canada, having the following specifications: a power-output of 40 Watt, wavelength 830 nm, drum diameter 286 mm, number of beams 192, spot size 10.6 x 2.5 micron (slowscan x fastscan), operating at 2450 dpi and an energy density of 275 mJ/m^2 on the plate at 150 rpm.

Gum solutions for developing

[0059] The following solutions were prepared for developing the printing plate precursors:

- Gum-solution-1: a solution of the following components:
  700 g demineralized water
  77.3 ml of DOWFAX 3B2 SURFACTANT SOLUTION, 45% (w/w) in water
  (available from DOW CHEMICAL)
  32.6 g trisodium citrate.2aqua
  9.8 g citric acid.1aqua
  adding demineralized water up to 1000 ml
  pH = 5 (+/- 0.20)
- Gum-solution-2: a solution of the following components:
  800 g demineralized water
  68 g KH_2PO_4.2aqua (available from CALDIC BELGIUM n.v.)
  22.5 ml of a 50% (w/w) solution of KOH in demineralized water
  23.2 ml of DOWFAX 3B2 SURFACTANT SOLUTION, 45% (w/w) in water
  (available from DOW CHEMICAL)
  adding demineralized water to obtain a solution of 1000 ml
  pH = 7 (+/- 0.20)

Development

[0060] After imaging, the plates were developed with a gum solution in a CRF85 processing apparatus (available from AGFA), fitted with a rotating brush, at a transport speed of 0.6 m/minute and for a dwell-time of 30seconds.

Background stain by LcH-measurement:

[0061] Background stain on the non-exposed areas of the printing plate increases the tendency of toning on the press. The background stain is determined by measuring the LcH-value using a GretagMacbeth SpectroEye (D65 - 2°-Abs -

No), supplied by GRETAG-MACBETH AG. Herein is

- La measure of lightness of an object, ranging from 0 (black) to 100 (white),
- C a measure of chroma (saturation), and represents the distance from the neutral axis, and
- H a measure of hue and is represented as an angle ranging from 0° to 360°. Angles that range from 0° to 90° are reds, oranges and yellows, from 90° to 180° are yellows, yellow-greens and greens, from 180° to 270° are greens, cyans (blue-greens) and blues, and from 270° to 360° are blues, purples, magentas, and return again to reds.

[0062] The lower the c-value the lower the stain: c < 4.0 means very low stain, c ranging between 4.0 and 6.0 means low stain, c ranging between 6.1 and 10 means moderate stain, c > 10 means heavy stain.

[0063] The results of the LcH-values for the plates, developed with the Gum-solution-1, are summarized in Table 4. For comparison, Table 4 summarizes also the LcH-values for the corresponding printing plate precursors in fresh condition, that is, without the high humidity shelf-life treatment. The results of the LcH-values for the plates, developed with the Gum-solution-2, are summarized in Table 5.

Table 4:

EXAMPLE (number)	PRECURSOR (number)	L (aged)	C (aged)	H (aged)	L (fresh)	C (fresh)	H (fresh)
INVENTION EXAMPLE 1	PRE-01	73.6	4.5	204.3	74.3	2.5	218.7
INVENTION EXAMPLE 2	PRE-02	73.9	4.8	206.0	75.7	2.4	223.0
INVENTION EXAMPLE 3	PRE-03	73.9	5.1	202.9	75.1	2.3	216.3
INVENTION EXAMPLE 4	PRE-04	72.3	7.0	201.0	75.1	2.3	214.8
INVENTION EXAMPLE 5	PRE-05	71.7	9.1	199.2	74.4	4.3	207.4
COMPARATIVE EXAMPLE 1	PRE-06	70.6	11.0	196.7	73.4	5.4	200.0
COMPARATIVE EXAMPLE 2	PRE-07	69.6	13.5	197.2	72.5	7.5	201.9
COMPARATIVE EXAMPLE 3	PRE-08	67.0	21.0	172.2	70.5	7.5	182.5
COMPARATIVE EXAMPLE 4	PRE-09	68.4	18.3	169.3	73.4	5.5	193.2
COMPARATIVE EXAMPLE 5	PRE-10	66.8	19.3	173.7	71.8	7.5	187.5

Table 5:

EXAMPLE (number)	PRECURSOR (number)	L (aged)	C (aged)	H (aged)
INVENTION EXAMPLE 6	PRE-01	75.0	2.3	180.0
INVENTION EXAMPLE 7	PRE-03	74.0	2.6	182.0

Printing run

[0064] The aged printing plate precursors of Invention Example 2 and 3 were developed after imaging with the Gum-solution-1 as described in Invention Example 2 and Invention Example 3. These plates were used as a printing master on a Heidelberg GTO52 printing press using K+E Skinnex Black, commercially available from BASF, as ink and 4 % Combifix

XL (commercially available from MICHAEL HUBER MUNCHEN GmbH) with 10% isopropanol as fountain solution. With these printing plates a high printing run length of 100 000 prints was obtained.

Conclusions

[0065] The Invention Examples 4 and 5 demonstrate that, after a shelf-life ageing of the precursor under high humidity condition, lower c-values are obtained, than when the grained and anodised aluminum plates were treated with a co-polymer of acrylic acid and vinylphosphonic acid, or polyvinylphosphonic acid (Comparative Examples 1 and 2) or potassium hexafluoro zirconate (Comparative Examples 3 to 5) was used. The background stain on the plates of Invention Examples 4 and 5 was reduced.

[0066] Invention Examples 1 to 3 demonstrate that, after ageing of the precursor under high humidity condition, very low c-values were obtained when the post-anodic treatment was carried out with polyacrylic acid. Invention Examples 1 to 3 exhibit no background stain.

[0067] Invention Examples 1 to 5 demonstrate also that, even for fresh printing plates (without the high humidity ageing), an improved clean-out is obtained when the support was post-anodic treated with a (co)polymer containing acrylic acid monomeric units in comparison with the Comparative Examples 1 to 5 where the support has been subjected to a post-anodic treatment with polyvinylphosphonic acid or a zirconium salt.

[0068] For the Invention Examples 2 and 3 was also demonstrated that a high printing run length without toning was obtained for these printing plates.

[0069] Invention Examples 6 and 7 demonstrate that, after ageing of the precursor under high humidity condition, still lower c-values were obtained when the post-anodic treatment was carried out with polyacrylic acid and when the gum solution in the developing step comprises an alkali-metal salt of a phosphate such as KH_2PO_4 instead of a sodium salt of citric acid. In these Invention Examples no background stain was observed.

Claims

1. A method of making a negative-working lithographic printing plate precursor comprising the steps of

(1) providing a grained and anodized aluminum support,
(2) treating the support with a hydrophilising agent,
(3) applying on said support a coating comprising hydrophobic thermoplastic polymer particles and an infrared light absorbing agent,

characterised in that said hydrophilising agent is a polymer containing acrylic acid monomeric units.

2. Method of making a negative-working lithographic printing plate comprising the steps of

(1) providing a lithographic printing plate precursor comprising

(i) a grained and anodized aluminum support which has been subjected to a post-anodic treatment with a hydrophilising agent and
(ii) on said support a coating comprising hydrophobic thermoplastic polymer particles and an infrared light absorbing agent;

(2) exposing said coating to heat, thereby inducing coalescence of said thermoplastic polymer particles at exposed areas of said coating;
(3) developing said precursor by applying a gum solution to said coating, thereby removing non-exposed areas of said coating from said support;

characterised in that said hydrophilising agent is a polymer containing acrylic acid monomeric units.

3. Method according to claim 1 or 2, wherein said polymer contains at least 30 mol% of acrylic acid monomeric units.

4. Method according to claims 1 or 2, wherein said polymer contains at least 50 mol% of acrylic acid monomeric units.

5. Method according to claims 1 or 2, wherein said polymer contains at least 75 mol% of acrylic acid monomeric units.

6. Method according to any one of preceding claims, wherein said treatment is carried out by applying an aqueous solution of said hydrophilising agent on said grained and anodised aluminum support by a coating, spraying or dipping technique.

7. Method according to claim 1, wherein said gum solution comprises an anionic surfactant and an inorganic salt.

8. Method according to claim 7, wherein said inorganic salt is an alkali-metal salt of a monobasic or dibasic phosphate.

9. Method according to claim 7 or 8, wherein said anionic surfactant is an alkali-metal salt of a substituted aryl sulphonate.

10. Method according to any of claims 1, 7, 8 or 9, wherein said gum solution has a pH-value between 6 and 8, preferably between 6.2 and 7.5.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 04 10 4832

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The present search report has been drawn up for all claims

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