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(54) **A method for preparing an aluminium foil for use as a support in lithographic printing plates**

(57) The present invention provides a method for preparing an aluminum foil comprising the steps of roughening an aluminum foil and subsequently anodizing said aluminum foil characterized in that after the roughening and before the anodization said aluminum foil is etched with an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l and subsequently with an acidic solution comprising strong acid in a total amount of at least 150 g/l. The present invention further provides a mono-sheet silver salt diffusion transfer material having as a support the aluminum foil obtained according to the above defined method.

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Description

1. Field of the invention.

5 The present invention relates to a method for preparing an aluminum foil suitable for use as a support for an imaging element for making a printing plate according to the silver salt diffusion transfer process.

2. Background of the invention.

10 The principles of the silver complex diffusion transfer reversal process, hereinafter called DTR-process, have been described e.g. in US-P-2,352,014 and in the book "Photographic Silver Halide Diffusion Processes" by André Rott and Edith Weyde - The Focal Press - London and New York, (1972).

In the DTR-process non-developed silver halide of an information-wise exposed photographic silver halide emulsion layer material is transformed with a so-called silver halide solvent into soluble silver complex compounds which are
15 allowed to diffuse into an image receiving element and are reduced therein with a developing agent, generally in the presence of physical development nuclei, to form a silver image having reversed image density values ("DTR-image") with respect to the black silver image obtained in the exposed areas of the photographic material.

A DTR-image bearing material can be used as a planographic printing plate wherein the DTR-silver image areas form the water-repellent ink-receptive areas on a water-receptive ink-repellent background.

20 The DTR-image can be formed in the image receiving layer of a sheet or web material which is a separate element with respect to the photographic silver halide emulsion material (a so-called two-sheet DTR element) or in the image receiving layer of a so-called single-support-element, also called mono-sheet element, which contains at least one photographic silver halide emulsion layer integral with an image receiving layer in waterpermeable relationship therewith. It is the latter mono-sheet version which is preferred for the preparation of offset printing plates by the DTR method.

25 Two types of the mono-sheet DTR offset printing plate exist. According to a first type disclosed in e.g. US-P-4,722,535 and GB-1,241,661 a support is provided in the order given with a silver halide emulsion layer and a layer containing physical development nuclei serving as the image-receiving layer. After information-wise exposure and development the imaged element is used as a printing plate without the removal of the emulsion layer.

30 According to a second type of mono-sheet DTR offset printing plate a hydrophilic support is provided in the order given with a layer of physical development nuclei and a silver halide emulsion layer. After information-wise exposure and development the imaged element is treated to remove the emulsion layer so that a support carrying a silver image is left which is used as a printing plate. Such type of lithographic printing plate is disclosed e.g. in US-P-3,511,656.

35 As a preferred support for the latter type of printing plates a roughened and anodized aluminum foil is used. Preferably roughening is followed by a chemical etching step using an aqueous solution containing an acid as disclosed in EP-A 567.178. Alternatively chemical etching may be carried out using an aqueous solution containing alkali as also disclosed in EP-A 567.178.

In order to obtain these printing plates according to the DTR process having good printing properties i.e. good ink acceptance in the image areas, no ink acceptance in the non-image areas called staining or toning and high printing
40 endurance it is required that the adhesion of the image receiving layer containing the physical development nuclei to the aluminum foil is firm. When the adhesion of the image receiving layer to the aluminum foil is poor a certain amount of silver image deposited in the image receiving layer will be removed together with the silver halide emulsion layer during rinsing of the imaging element so that the actual yield or amount of silver deposited in the image receiving layer will be low and as a consequence the printing endurance may be low. Furthermore if the adhesion of the image receiving layer to the aluminum foil is low the silver image will also be worn away more rapidly during printing.

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3. Summary of the invention.

It is an object of the present invention to provide a method for preparing an aluminum foil having a high adhesion for an image receiving layer containing physical development nuclei.

50 It is another object of the present invention to provide an aluminum based mono-sheet DTR material for preparing a lithographic printing plate having good printing properties.

Further objects of the present invention will be clear from the description hereinafter.

According to the present invention there is provided a method for preparing an aluminum foil comprising the steps of roughening an aluminum foil and subsequently anodizing said aluminum foil characterized in that after the roughening
55 and before the anodization said aluminum foil is etched with an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l and subsequently with an acidic solution comprising strong acid in a total amount of at least 150 g/l.

According to the present invention there is also provided a mono-sheet DTR material comprising on the aluminum support obtained by the above described method in the order given an image receiving layer containing physical development nuclei and a silver halide emulsion layer being in water permeable contact with each other.

4. Detailed description of the invention.

According to the present invention it has been found that etching of an aluminum foil after the roughening and before the anodization with an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l and subsequently with an acidic solution comprising strong acid in a total amount of at least 150 g/l improves the adhesion of an image receiving layer containing physical development nuclei to the aluminum foil as revealed from the increased amount of silver precipitated in the image receiving layer when the aluminum foil provided with an image receiving layer is used in a DTR-process.

In DE-A-2251382 a process for etching an aluminum foil is described consisting of an alkaline etching by means of a 10% aqueous sodium hydroxide solution followed by an acidic etching by means of a 20% nitric acid solution. Said etching is used in order to avoid the blackening of grained aluminum foil during anodization and does not mention the problem the present application tries to solve. Furthermore the concentration on strong base is clearly higher than suitable for the present application, the alkaline etching being too aggressive.

As mentioned above a DTR-image on a hydrophilic background i.e. on a hydrophilic aluminum foil can be used in lithographic printing. Because of the improved adhesion of the nuclei to the aluminum foil prepared according to the invention more silver is deposited in the image receiving layer and a silver image is obtained with an improved wear resistance and as a consequence high printing endurance can be obtained.

According to the present invention the roughening of the aluminum foil is followed by a chemical etching step using an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l. This chemical etching is preferably carried out at a temperature in the range from 15°C to 50°C, more preferably in a temperature range from 20°C to 40°C. When too low temperatures during this chemical etching are employed a poor adhesion of the image receiving layer to the aluminum foil may result.

Suitable alkali for use in this aqueous etch solution are inorganic strong alkali, strong alkali being alkali with a pK_a of at least 13. Examples of alkali that are particularly suitable are e.g. NaOH, KOH etc. or mixtures thereof. Salts of a strong alkali and a weak acids may also be used in admixture with strong alkali e.g. sodium gluconate. The total amount of alkali in this aqueous etch solution ranges preferably from 4 g/l to 50 g/l, more preferably from 5 g/l to 25 g/l. The duration of this chemical etching is preferable between 3s and 5min. and more preferably between 5s and 4min.

According to the present invention the chemical etching using an aqueous solution comprising strong alkali is followed by a chemical etching step using an aqueous solution comprising a strong acid. This acidic chemical etching is preferably carried out at a temperature of at least 30°C more preferably at least 40°C and most preferably at least 50°C. When too low temperatures during this acidic chemical etching are employed a poor adhesion of the image receiving layer to the aluminum foil may result. There is no specific upper limit as to the temperature of this acidic chemical etching but for convenience the temperature will generally be kept below the boiling point of the solution preferably below 90°C.

Suitable acids for use in the aqueous acidic etch solution are preferably strong inorganic acids, strong acids being acids with a pK_a of at most 1. Examples of acids that are particularly suitable are e.g. H_2SO_4 , HCl, HNO_3 , HF, H_3PO_4 etc. or mixtures thereof. Weak acids may also be used in admixture with strong acids. The total amount of acid in the aqueous acidic etch solution is preferably at least 200g/l and more preferably at least 250g/l. The duration of chemical etching is preferably between 3s and 5min. and more preferably between 4s and 4min.

Between the etching with an alkaline solution and the etching with an acidic solution the aluminum foil may be rinsed with demineralised water preferably at a temperature in the range of 15-30°C.

The aluminum support of the imaging element for use in accordance with the present invention can be made of pure aluminum or of an aluminum alloy, the aluminum content of which is at least 95%. The thickness of the support usually ranges from about 0.13 to about 0.50 mm.

The preparation of aluminum or aluminum alloy foils for lithographic offset printing comprises the following steps : graining, anodizing, and optionally a posttreatment of the foil.

Graining and anodization of the foil are necessary to obtain a lithographic printing plate that allows to produce high-quality prints in accordance with the present invention. Posttreating is not necessary but may still improve the printing results. Preferably the aluminum foil has a roughness with a CLA value between 0.2 and 1.5 μm , an anodization layer with a thickness between 0.4 and 2.0 μm and is posttreated with an aqueous bicarbonate solution.

According to the present invention the roughening of the aluminum foil can be performed according to the methods well known in the prior art.

The surface of the aluminum substrate can be roughened either by mechanical, chemical or electrochemical graining or by a combination of these to obtain a satisfactory adhesiveness of a silver halide emulsion layer to the aluminum support and to provide a good water retention property to the non-printing areas that will form the non-printing areas on the plate surface.

Mechanical graining can be performed by e.g. sand blasting, ball graining, wire graining, brush graining, slurry graining or a combination of these, etc..

Chemical graining can be done e.g. by alkaline etching as disclosed in Jap. Patent Application N°. 61304/76, with a saturated aqueous solution of an aluminum salt of a mineral acid, etc..

The electrochemical graining process is preferred because it can form a uniform surface roughness having a large average surface area with a very fine and even grain which is commonly desired when used for lithographic printing plates.

To obtain a finely grained surface topography the optimum concentration and temperature of the electrolytic solution, the current form and density must be chosen.

According to the present invention electrochemical graining can be conducted in a hydrochloric and/or nitric acid containing electrolyte solution using an alternating or direct current. Other aqueous solutions that can be used in the electrochemical graining are e.g. acids like HNO_3 , H_2SO_4 , H_3PO_4 , that if desired, contain additionally one or more corrosion inhibitors such as $\text{Al}(\text{NO}_3)_3$, AlCl_3 , boric acid, chromic acid, sulfates, chlorides, nitrates, monoamines, diamines, aldehydes, phosphates, H_2O_2 , etc..

Electrochemical graining in connection with the present invention can be performed using single-phase and three-phase alternating current. Alternating current waves can be a sine wave, a square wave, trapezoidal wave, etc.. The anodic charge may be greater or lower than the cathodic charge. The voltage applied to the aluminum plate is about 1-60 V and preferably 10-35 V. A current density of 3-150 Amp/dm² is employed for 5-240 seconds. The temperature of the electrolytic graining solution may vary from 5-50°C. Electrochemical graining is carried out preferably with an alternating current from 10 Hz to 300 Hz.

Mechanical and electrochemical methods may be combined as disclosed in US Pat. N°. 4,476,006 and 4,477,317.

Roughening in the present invention is preferably carried out so that an average center line roughness (Ra) of the surface may range from 0,3 to 1,3 µm.

The roughening is preferably preceded by a degreasing treatment mainly for removing greasy substances from the surface of the aluminum foil.

Therefore the aluminum foil may be subjected to a degreasing treatment with a surfactant and/or an aqueous alkaline solution to thereby remove rolling oil, dust, rust and other impurities on the surface thereof. Degreasing can be performed by a 2-step treatment either treating the aluminum foil with an alkaline solution followed by a desmutting in an acidic solution or degreasing in an acidic solution followed by an alkaline desmutting. Acidic solutions preferably contain chromic acid, phosphoric acid or sulphuric acid, and usable alkaline solutions may contain NaOH, KOH, etc..

According to the present invention after the second chemical etching by means of an aqueous solution containing strong acid in a total amount of at least 150 g/l the aluminum foil is anodized which may be carried out as follows.

An electric current is passed through the grained aluminum foil immersed as an anode in a solution containing sulfuric acid, phosphoric acid, oxalic acid, chromic acid or organic acids such as sulfamic, benzosulfonic acid, etc. or mixtures thereof. An electrolyte concentration from 1 to 70 % by weight can be used at a temperature in the range from 0 - 70°C, preferably at a temperature in the range from 35 - 60°C, more preferably at a temperature in the range from 40 - 50°C. The anodic current density may vary from 1 - 50 A/dm² and the voltage within the range 1 - 100 V to obtain an anodized film weight of 1 - 8 g/m² $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The anodized aluminum foil may subsequently be rinsed with demineralised water at a temperature in the range of 10 - 80°C.

After the anodizing step a posttreatment e.g. sealing may be applied to the anodic surface. Sealing of the pores of the aluminum oxide layer formed by anodization is a technique known to those skilled in the art of aluminum anodization. This technique has been described in e.g. the "Belgisch-Nederlands tijdschrift voor Oppervlaktetechnieken van materialen", 24ste jaargang/januari 1980, under the title "Sealing-kwaliteit en sealing-controle van geanodiseerd Aluminium". Different types of sealing of the porous anodized aluminum surface exist.

Preferably, said posttreatment is performed by treating a grained and anodized aluminum support with an aqueous solution containing a bicarbonate as disclosed in EP-A 567.178, which therefor is incorporated herein by reference.

Preferably each of the above described steps is separated by a rinsing step to avoid contamination of the liquid used in a particular step with that of the preceding step.

To promote the image sharpness and, as a consequence thereof, the sharpness of the final printed copy, the anodization layer may be coloured in the mass with an antihalation dye or pigment e.g. as described in JA-Pu-58-14,797.

Subsequent to the preparation of the aluminum foil as described above the aluminum foil may be immediately coated with a solution containing the physical development nuclei or may be coated with said solution at a later stage.

The image receiving layer containing physical development nuclei is preferably free of hydrophilic binder but may comprise amounts upto e.g. 80% by weight of the total weight of said layer of a hydrophilic colloid e.g. polyvinyl alcohol to improve the hydrophilicity of the surface.

Preferred development nuclei for use in accordance with the present invention are sulphides of heavy metals e.g. sulphides of antimony, bismuth, cadmium, cobalt, lead, nickel, palladium, platinum, silver, and zinc. Especially suitable development nuclei in connection with the present invention are palladium sulphide nuclei. Other suitable development nuclei are salts such as e.g. selenides, polyselenides, polysulphides, mercaptans, and tin (II) halides. Heavy metals, preferably silver, gold, platinum, palladium, and mercury can be used in colloidal form.

The aluminum support according to the present invention is especially suited for preparing a mono-sheet DTR material. According to the method of the present invention for obtaining a mono-sheet DTR material an aluminum foil prepared as described above and provided with an image receiving layer is provided with a photosensitive layer in water permeable contact with said image receiving layer.

Layers being in waterpermeable contact with each other are layers that are contiguous to each other or only separated from each other by (a) waterpermeable layer(s). The nature of a waterpermeable layer is such that it does not substantially inhibit or restrain the diffusion of water or of compounds contained in an aqueous solution e.g. developing agents or the complexed silver.

The photosensitive layer used according to the present invention may be any layer comprising a hydrophilic colloid binder and at least one silver halide emulsion, at least one of the silver halide emulsions being photosensitive.

The photographic silver halide emulsion(s) used in accordance with the present invention can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

For use according to the present invention the silver halide emulsion or emulsions preferably consist principally of silver chloride while a fraction of silver bromide may be present ranging from 1 mole % to 40 mole %. Most preferably a silver halide emulsion containing at least 70 mole% of silver chloride is used.

The average size of the silver halide grains may range from 0.10 to 0.70 μm , preferably from 0.25 to 0.45 μm .

Preferably during the precipitation stage iridium and/or rhodium containing compounds or a mixture of both are added. The concentration of these added compounds ranges from 10^{-8} to 10^{-3} mole per mole of AgNO_3 , preferably between 10^{-7} and 10^{-5} mole per mole of AgNO_3 .

The emulsions can be chemically sensitized e.g. by adding sulphur-containing compounds during the chemical ripening stage e.g. allyl isothiocyanate, allyl thiourea, and sodium thiosulphate. Also reducing agents e.g. the tin compounds described in BE-P 493,464 and 568,687, and polyamines such as diethylene triamine or derivatives of aminomethane-sulphonic acid can be used as chemical sensitizers. Other suitable chemical sensitizers are noble metals and noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium. This method of chemical sensitization has been described in the article of R.KOSLOWSKY, Z. Wiss. Photogr. Photophys. Photochem. 46, 65-72 (1951).

Apart from negative-working silver halide emulsions that are preferred for their high photosensitivity, use can be made also of direct-positive silver halide emulsions that produce a positive silver image in the emulsion layer(s) and a negative image on the image-receiving layer.

Suitable direct positive silver halide emulsions for use in accordance with the present invention are silver halide emulsions that have been previously fogged or that mainly form an internal latent image.

Internal latent image-type silver halide emulsions that can be used in accordance with the present invention have been described in e.g. US-A 2,592,250, 3,206,313, 3,271,157, 3,447,927, 3,511,662, 3,737,313, 3,761,276, GB-A 1,027,146, and JA Patent Publication No. 34,213/77. However, the silver halide emulsions used in the present invention are not limited to the silver halide emulsions described in these documents.

The other type of direct positive type silver halide emulsions for use in accordance with the present invention, which is of the previously fogged type, may be prepared by overall exposing a silver halide emulsion to light and/or by chemically fogging a silver halide emulsion. Chemical fog specks may be formed by various methods for chemical sensitization.

Chemical fogging may be carried out by reduction or by a compound which is more electropositive than silver e.g. gold salts, platinum salts, iridium salts etc., or a combination of both. Reduction fogging of the silver halide grains may occur by high pH and/or low pAg silver halide precipitation or digestion conditions e.g. as described by Wood J. Phot. Sci. 1 (1953), 163 or by treatment with reducing agents e.g. tin(II) salts which include tin(II)chloride, tin complexes and tin chelates of (poly)amino(poly)carboxylic acid type as described in British Patent 1,209,050, formaldehyde, hydrazine, hydroxylamine, sulphur compounds e.g. thiourea dioxide, phosphonium salts e.g. tetra(hydroxymethyl)-phosphonium chloride, polyamines e.g. diethylenetriamine, bis(p-aminoethyl)sulphide and its water-soluble salts, hydrazine derivatives, alkali arsenite, amine borane etc. or mixtures thereof.

When fogging of the silver halide grains occurs by means of a reducing agent e.g. thiourea dioxide and a compound of a metal more electropositive than silver especially a gold compound, the reducing agent is preferably used initially and the gold compound subsequently. However, the reverse order can be used or both compounds can be used simultaneously.

In addition to the above described methods of chemically fogging chemical fogging can be attained by using said fogging agents in combination with a sulphur-containing sensitizer, e.g. sodium thiosulphate or a thiocyanic acid compound e.g. potassium thiocyanate.

The silver halide emulsions of the DTR-element can be spectrally sensitized according to the spectral emission of the exposure source for which the DTR element is designed.

Suitable sensitizing dyes for the visible spectral region include methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for this purpose include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

In the case of a conventional light source, e.g. tungsten light, a green sensitizing dye is needed. In case of exposure by an argon ion laser a blue sensitizing dye is incorporated. In case of exposure by a red light emitting source, e.g. a LED or a HeNe laser a red sensitizing dye is used. In case of exposure by a semiconductor laser special spectral sensitizing dyes suited for the near infra-red are required. Suitable infra-red sensitizing dyes are disclosed in i.a. US-P 2,095,854, 2,095,856, 2,955,939, 3,482,978, 3,552,974, 3,573,921, 3,582,344, 3,623,881 and 3,695,888.

A preferred blue sensitizing dye, green sensitizing dye, red sensitizing dye and infra-red sensitizing dye in connection with the present invention are described in EP-A 554,585.

To enhance the sensitivity in the red or near infra-red region use can be made of so-called supersensitizers in combination with red or infra-red sensitizing dyes. Suitable supersensitizers are described in Research Disclosure Vol 289, May 1988, item 28952. The spectral sensitizers can be added to the photographic emulsions in the form of an aqueous solution, a solution in an organic solvent or in the form of a dispersion.

The silver halide emulsions may contain the usual emulsion stabilizers. Suitable emulsion stabilizers are azaindenes, preferably tetra- or penta-azaindenes, especially those substituted with hydroxy or amino groups. Compounds of this kind have been described by BIRR in Z. Wiss. Photogr. Photophys. Photochem. 47, 2-27 (1952). Other suitable emulsion stabilizers are i.a. heterocyclic mercapto compounds.

The silver halide emulsion layers usually contains gelatin as hydrophilic colloid binder. Mixtures of different gelatins with different viscosities can be used to adjust the rheological properties of the layer. But instead of or together with gelatin, use can be made of one or more other natural and/or synthetic hydrophilic colloids, e.g. albumin, casein, zein, polyvinyl alcohol, alginic acids or salts thereof, cellulose derivatives such as carboxymethyl cellulose, modified gelatin, e.g. phthaloyl gelatin etc.

Preferably the gelatin layer(s) is (are) substantially unhardened. Substantially unhardened means that when such gelatin layer is coated on a subbed polyethylene terephthalate film base at a dry thickness of 1.2 g/m², dried for 3 days at 57 °C and 35% R.H. and dipped in water of 30 °C, said gelatin layer is dissolved for more than 95 % by weight within 5 minutes.

The silver halide emulsions may contain pH controlling ingredients. Preferably at least one gelatin containing layer is coated at a pH value not below the iso-electric point of the gelatin to avoid interactions between said gelatin containing coated layer and the hereafter mentioned intermediate layer. More preferably the gelatin layer contiguous to said intermediate layer is coated at a pH value not below the iso-electric point of the gelatin. Most preferably all the gelatin containing layers are coated at a pH value not below the iso-electric point of their gelatin. Other ingredients such as antifogging agents, development accelerators, wetting agents, and hardening agents for gelatin may be present. The silver halide emulsion layer may comprise light-screening dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes are described in i.a. US-P 4,092,168, US-P 4,311,787 and DE-P 2,453,217.

More details about the composition, preparation and coating of silver halide emulsions suitable for use in accordance with the present invention can be found in e.g. Product Licensing Index, Vol. 92, December 1971, publication 9232, p. 107-109.

Preferably, the imaging element also comprises an intermediate layer between the image receiving layer on the hydrophilic surface of a support and the photosensitive layer (packet) to facilitate the removal of said layer (packet) thereby uncovering the silver image formed in the image receiving layer by processing the imaging element.

In one embodiment, the intermediate layer is a water-swellaable intermediate layer coated at a ratio of 0.01 to 2.0 g/m² and comprising at least one non-proteinic hydrophilic film-forming polymer e.g. polyvinyl alcohol and optionally comprising an antihalation dye or pigment as disclosed in EP-A-410500.

In another embodiment, the intermediate layer is a layer comprising hydrophobic polymer beads having an average diameter not lower than 0.2 µm and having been prepared by polymerization of at least one ethylenically unsaturated monomer. Preferably, said intermediate layer in dry condition comprises said hydrophobic polymer beads in an amount of up to 80% of its total weight. Further details are disclosed in EP-A-483415.

A supplemental intermediate layer, which may be present between said silver halide emulsion containing layer and said water-swellaable intermediate layer or said intermediate layer comprising hydrophobic polymer beads may incorporate one or more ingredients such as i.a. antihalation dyes or pigment, developing agents, silver halide solvents, base precursors, and anticorrosion substances.

The silver halide emulsion layer and optional other layers may be coated to the aluminum support according to the present invention provided with an image receiving layer using commonly applied coating techniques as slide hopper coating or curtain coating. Alternatively these layers may be first coated to a temporary support e.g. a polyester film and subsequently laminated to the aluminum support as disclosed in EP-A-410500.

When the imaging element is prepared by laminating a layer packet comprising a photosensitive layer onto the image receiving layer the intermediate layer(s) are provided on the photosensitive layer(s), the water-swellaable intermediate layer or the intermediate layer comprising hydrophobic polymer beads having an average diameter not lower than 0.2 µm and having been prepared by polymerization of at least one ethylenically unsaturated monomer being the upper layer.

Although the aluminum support according to the present invention is mainly intended as a support for a monosheet DTR material it is equally well suited for use as a receiving material in a two-sheet DTR process.

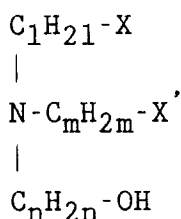
According to the present invention the imaging element can be information-wise exposed in an apparatus according to its particular application. A wide choice of cameras for exposing the photosensitive silver halide emulsion exists on the market. Horizontal, vertical and darkroom type cameras and contact-exposure apparatus are available to suit any particular class of reprographic work. The imaging element in accordance with the present invention can also be exposed with the aid of i.a. laser recorders and cathode rays tubes.

According to the present invention the development and diffusion transfer of the information-wise exposed imaging element in order to form a silver image in said photosensitive layer and to allow unreduced silver halide or complexes formed thereof to diffuse image-wise from the photosensitive layer to said image receiving layer to produce therein a silver image, are effected with the aid of an aqueous alkaline solution in the presence of (a) developing agent(s), and (a) silver halide solvent(s). The developing agent(s) and/or the silver halide solvent(s) can be incorporated in the aqueous alkaline solution and/or in the imaging element.

Preferably a silver halide solvent in the aqueous alkaline solution is used in an amount between 0.05% by weight and 5% by weight and more preferably between 0.5% by weight and 2% by weight. The silver halide solvent, which acts as a complexing agent for silver halide, preferably is a water-soluble thiosulphate or thiocyanate e.g. sodium, potassium, or ammonium thiosulphate and sodium, potassium, or ammonium thiocyanate.

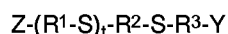
Further silver halide solvents that can be used in connection with the present invention are e.g. sulphite, amines, 2-mercaptobenzoic acid, cyclic imide compounds such as e.g. uracil, 5,5-dialkylhydantoins, alkyl sulfones and oxazolones.

Further silver halide solvents for use in connection with the present invention are alkanolamines. Examples of alkanolamines that may be used in connection with the present invention correspond to the following formula:



wherein X and X' independently represent hydrogen, a hydroxyl group or an amino group, l and m represent 0 or integers of 1 or more and n represents an integer of 1 or more. Said alkanolamines may be present in the alkaline processing liquid in a concentration preferably between 0.1% and 5% by weight. However part or all of the alkanolamine can be present in one or more layers of the imaging element.

Still other preferred further silver halide solvents for use in connection with the present invention are thioethers. Preferably used thioethers correspond to the following general formula:



wherein Z and Y each independently represents hydrogen, an alkyl group, an amino group, an ammonium group, a hydroxyl, a sulfo group, a carboxyl, an aminocarbonyl or an aminosulfonyl, R¹, R² and R³ each independently represents an alkylene that may be substituted and optionally contain an oxygen bridge and t represents an integer from 0 to 10. Examples of thioether compounds corresponding to the above formula are disclosed in e.g. US-P-4.960.683 and EP-A 554,585.

Still further suitable silver halide solvents are 1,2,4-triazolium-3-thiolates, preferably 1,2,4-triazolium-3-thiolates substituted with at least one substituent selected from the group consisting of a C₁-C₈ alkyl group that contains at least 3 fluorine atoms, a C₄-C₁₀ hydrocarbon group and a 4-amino group substituted with a C₁-C₈ alkyl group that contains at least 3 fluorine atoms and/or a C₄-C₁₀ hydrocarbon group.

Combinations of different silver halide solvents can be used and it is also possible to incorporate at least one silver halide solvent into a suitable layer of the imaging element and to add at least one other silver halide solvent to the developing solution.

The alkaline processing liquid may also contain (a) developing agent(s). In this case the alkaline processing liquid is called a developer. On the other hand some or all of the developing agent(s) may be present in one or more layers of the photographic material or imaging element. When all of the developing agents are contained in the imaging element the alkaline processing liquid is called an activator or activating liquid.

Silver halide developing agents for use in accordance with the present invention are preferably of the p-dihydroxybenzene type, e.g. hydroquinone, methylhydroquinone or chlorohydroquinone, preferably in combination with an auxiliary developing agent being a 1-phenyl-3-pyrazolidone-type developing agent and/or p-monomethylaminophenol. Particularly useful auxiliary developing agents are the 1-phenyl-3-pyrazolidones. Even more preferred, particularly when they are incorporated into the photographic material are 1-phenyl-3-pyrazolidones of which the aqueous solubility is increased by a hydrophilic substituent such as e.g. hydroxy, amino, carboxylic acid group, sulphonic acid group etc.. Examples of 1-phenyl-3-pyrazolidones substituted with one or more hydrophilic groups are e.g. 1-phenyl-4,4-dimethyl-2-hydroxy-3-pyrazolidone, 1-(4-carboxyphenyl)-4,4-dimethyl-3-pyrazolidone etc.. However other developing agents can be used.

Preferred amounts of the hydroquinone-type developing agents are in the range of 0.05 mole to 0.40 mole per litre and preferred amounts of secondary developing agent(s) in the range of 1.8×10^{-3} to 2.0×10^{-1} mole per litre.

The aqueous alkaline solution in accordance with the present invention may further comprise sulphite e.g. sodium sulphite in an amount ranging from 40 g to 180 g per liter, preferably from 60 to 160 g per liter in combination with another silver halide solvent.

The quantitative ranges given for the developing agents, silver halide solvents, and sulphite apply to the amount of these compounds present as solutes in the aqueous alkaline solution during the DTR-processing, whether these compounds make part of the aqueous alkaline solution or were dissolved from the layers containing them upon application thereto of the aqueous alkaline solution.

The aqueous alkaline solution suitable for use according to the present invention preferably comprises aluminum ions in an amount of at least 0.3 g/l, more preferably in an amount of at least 0.6 g/l in order to prevent sticking of the emulsion layer to the transporting rollers when the emulsion is swollen with the aqueous alkaline solution.

The alkaline processing liquid preferably has a pH between 9 and 14 and more preferably between 10 and 13, but depends on the type of silver halide emulsion material to be developed, intended development time, and processing temperature.

The processing conditions such as temperature and time may vary within broad ranges provided the mechanical strength of the materials to be processed is not adversely influenced and no decomposition takes place.

The pH of the alkaline processing liquid may be established by an organic or inorganic alkaline substance or a combination thereof. Suitable inorganic alkaline substances are e.g. hydroxides of sodium and potassium, alkali metal salts of phosphoric acid and/or silicic acid e.g. trisodium phosphate, orthosilicates, metasilicates, hydrodisilicates of sodium or potassium, and sodium carbonate etc.. Suitable organic alkaline substances are e.g. alkanolamines. In the latter case the alkanolamines will provide or help providing the pH and serve as a silver halide complexing agent.

The aqueous alkaline solution may further comprise hydrophobizing agents for improving the hydrophobicity of the silver image obtained in the image receiving layer. Generally these compounds contain a mercapto group or thiolate group and one or more hydrophobic substituents. Particularly preferred hydrophobizing agents are mercapto-1,3,4-thiadiazoles as described in DE-A 1,228,927 and in US-P 4,563,410, 2-mercapto-5-heptyl-oxa-3,4-diazole and long chain (at least 5 carbon atoms) alkyl substituted mercaptotetrazoles. The hydrophobizing agents can be used alone or in combination with each other.

These hydrophobizing compounds can be added to the aqueous alkaline solution in an amount of preferably 0.1 to 3 g per litre and preferably in admixture with 1-phenyl-5-mercaptotetrazole the latter compound may be used in amounts of e.g. 50 mg to 1.2 g per litre of solution, which may contain a minor amount of ethanol to improve the dissolution of said compounds.

The aqueous alkaline solution may comprise other ingredients such as e.g. oxidation preservatives, calcium-sequestering compounds, anti-sludge agents, and hardeners including latent hardeners.

Regeneration of the aqueous alkaline solution according to known methods is, of course, possible, whether the solution incorporates developing agent(s) and/or silver halide solvent(s) or not.

The development may be stopped - though this is often not necessary - with a so-called stabilization liquid, which actually is an acidic stop-bath having a pH preferably in the range from 5 to 7.

Buffered stop bath compositions comprising a mixture of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate and having a pH in said range are preferred.

The development and diffusion transfer can be initiated in different ways e.g. by rubbing with a roller, by wiping with an absorbent means e.g. with a plug of cotton or sponge, or by dipping the material to be treated in the liquid composition. Preferably, they proceed in an automatically operated apparatus. They are normally carried out at a temperature in the range of 18°C to 30°C and in a time from 5 s to 5 min.

After formation of the silver image on the hydrophilic surface of a support an excess of aqueous alkaline solution still present on the base may be eliminated, preferably by guiding the foil through a pair of squeezing rollers.

The silver image thus obtained in the layer of physical development nuclei is subsequently uncovered by treating the imaging element to remove all the layers above the layer containing physical development nuclei, thereby exposing the imaged surface of the hydrophilic support.

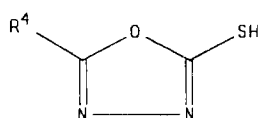
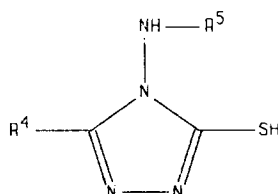
According to a particularly preferred embodiment of the present invention the silver image in the layer of physical development nuclei is uncovered by washing off all the layers above the layer containing physical development nuclei with rinsing water.

The temperature of the rinsing water may be varied widely but is preferably between 30 °C and 50 °C, more preferably between 35°C and 45°C.

The imaged surface of the hydrophilic surface of a support can be subjected to a chemical treatment that increases the hydrophilicity of the non-silver image parts and the oleophilicity of the silver image

This chemical after-treatment is preferably carried out with a lithographic composition often called finisher comprising at least one compound enhancing the ink-receptivity and/or lacquer-receptivity of the silver image and at least one compound that improves the ink-repelling characteristics of the hydrophilic surface.

Suitable ingredients for the finisher are e.g. organic compounds containing a mercapto group such as the hydrophobizing compounds referred to hereinbefore for the alkaline solution. Preferred compounds correspond to one of the following formulas:



wherein R⁵ represents hydrogen or an acyl group, R⁴ represents alkyl, aryl or aralkyl. Most preferably used compounds are compounds according to one of the above formulas wherein R⁴ represents an alkyl containing 3 to 16 C-atoms. Said (a) hydrophobizing agent(s) is (are) comprised in the finisher preferably in a total concentration between 0.1 g/l and 10 g/l, more preferably in a total concentration between 0.3 g/l and 3 g/l.

Additives improving the oleophilic ink-repellency of the hydrophilic surface areas are e.g. carbohydrates such as acidic polysaccharides like gum arabic, carboxymethylcellulose, sodium alginate, propylene glycol ester of alginic acid, hydroxyethyl starch, dextrin, hydroxyethylcellulose, polyvinyl pyrrolidone polystyrene sulphonic acid, polyglycols being the reaction products of ethyleneoxide and/or propyleneoxide with water or an alcohol and polyvinyl alcohol. Optionally, hygroscopic substances e.g. sorbitol, glycerol, tri(hydroxyethyl)ester of glycerol, and turkey red oil may be added.

Furthermore (a) surface-active compound(s) is preferably also added to the finisher. The concentration thereof may vary within broad ranges provided the finisher shows no excessive degree of foaming when plates are finished. Preferred surface-active compound are anionic or non-ionic surface-active compound.

A suitable finisher as disclosed in US-A-4.563.410 is a composition comprising a solution of a mercaptotriazole in a solution of polyethylene oxide with a molecular weight of 4,000. Further suitable finishers have been described in i.a. US-A 4.062.682.

At the moment the treatment with the finisher is started the surface carrying the silver pattern may be in dry or wet state. In general, the treatment with the finisher does not take long, usually not longer than about 30 seconds and it may be carried out immediately after the processing and uncovering steps, preferably at a temperature of the finisher in the range from 30°C to 60°C.

The finisher can be applied in different ways such as by rubbing with a roller, by wiping with an absorbent means e.g. with a plug of cotton or sponge, or by dipping the material to be treated in the finisher. The image-hydrophobizing step of the printing plate may also proceed automatically by conducting the printing plate through a device having a narrow channel filled with the finisher and conveying the printing plate at the end of the channel between two squeezing rollers removing the excess of liquid.

As soon as the hydrophilic surface of a support carrying the silver image has been treated with the finisher, it is ready to be used as a printing plate.

The following example illustrates the present invention without however, limiting it thereto. All parts, percentages and ratios are by weight unless otherwise indicated.

EXAMPLE

A 0,30 mm thick aluminum foil (AA 1050) was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 0,5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m² to form a surface topography with an average center-line roughness Ra of 0,5 µm. After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water of 25°C for 30 s. The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid to form an anodic oxidation film of 2.60 g/m² of Al₂O₃.H₂O, then washed with demineralised water, subsequently posttreated with a solution containing 20 g/l of sodium bicarbonate at 40 °C for 30 s and finally dried. The thus obtained aluminum foil is called support A.

A support B was prepared similar to the above procedure with the difference that the aluminum foil was etched with an aqueous solution containing 5 g/l of sodium hydroxide at 25°C for 20 seconds and rinsed with demineralized water of 25°C for 30 s.

A support C was made similar to the procedure disclosed for support A, with the difference that after the aluminum foil was etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water of 25°C for 30 s, it was subsequently etched with an aqueous solution containing 5 g/l of sodium hydroxide at 25°C for 20 seconds and rinsed with demineralised water of 25°C for 30 s.

A support D was made in the same way as described for support B with the difference that after the aluminum foil was etched with an aqueous solution containing 5 g/l of sodium hydroxide at 25°C for 20 seconds and rinsed with demineralized water of 25°C for 30 s, it was etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralised water of 25°C for 30 s.

The 4 obtained aluminum supports were each coated with a silver-receptive stratum containing 1.1 mg/m² PdS as physical development nuclei.

An intermediate layer was then provided on the dry silver-receptive stratum from an aqueous composition in such a way that the resulting dried layer had a weight of 0.5 g of polymethyl methacrylate beads per m², said composition comprising:

a 20 % dispersion of polymethyl methacrylate beads in a mixture of equal volumes of water and ethanol having an average diameter of 1.0 µm	50 ml
Helioechtpapierrot BL (trade mark for a dye sold by BAYER AG, D-5090 Leverkusen, West-Germany)	2.5 g
saponine	2.5 g
sodium oleylmethyltauride	1.25 g
demineralized water	300 ml
(pH-value : 5.6)	

Finally a substantially unhardened photosensitive negative-working cadmium-free gelatin silver chlorobromiodide emulsion layer (97.98 / 2 / 0.02 mol%) containing 1 mmole/mole AgX of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was coated on the intermediate layer, the silver halide being provided in an amount corresponding to 2.40 g of silver nitrate per m² and the gelatin content of the emulsion layer being 1.58 g/m², consisting of 0.7 g/m² of a gelatin with a viscosity of 21 mPa.s and the remainder of a gelatin with a viscosity of 14 mPa.s

The 4 obtained unexposed mono-sheet DTR materials were immersed for 8 s at 25°C in a freshly made developing solution having the following ingredients:

carboxymethylcellulose	4 g
sodium hydroxide	22.5 g
anhydrous sodium sulphite	120 g
hydroquinone	20 g
1-phenyl-4-methyl-3-pyrazolidone	6 g
potassium bromide	0.75 g
anhydrous sodium thiosulphate	8 g
ethylene diamine tetraacetic acid tetrasodium salt	2 g
demineralized water to make	1000 ml
pH (24°C) = 13	

The initiated diffusion transfer was allowed to continue for 30 s to form a silver layer on each of the 4 supports.

To remove the developed silver halide emulsion layer and the swollen intermediate layer from the aluminum foils the developed mono-sheet DTR materials were rinsed for 30 s with a water jet at 30°C.

The amount of silver deposited (silver yield) in the image receiving layer was then measured using an analytical X-ray Fluorescence Spectrophotometer PHILIPS 1400 (commercially available from Philips). The results obtained for each of the 4 DTR materials are given in table 1.

Table 1

Support	Silver yield ^{a)}	Silver yield ^{b)}	Δ Silver yield
A	1,60 g/m ²	1,51 g/m ²	0,09 g/m ²
B	1,43 g/m ²	1,30 g/m ²	0,13 g/m ²
C	1,48 g/m ²	1,41 g/m ²	0,07 g/m ²
D	1,70 g/m ²	1,63 g/m ²	0,06 g/m ²

Remarks :

a) Silver yield in the image receiving layer after treatment with the finisher.

b) Silver yield in the image receiving layer after rubbing the finished plate with a plug of cotton made wet with water.

From the above it can be seen that when the aluminum foil after the roughening has been etched with an alkaline solution comprising 5 g/l of sodium hydroxyde and subsequently with an acidic solution comprising 300 g/l of sulfuric acid (support D according to the invention) , the silver yield is improved in comparison with the case where the aluminum foil is only etched with an acidic solution comprising 300 g/l of sulfuric acid (comparison support A) and much improved in comparison with the cases where the aluminum foil is only etched with an alkaline solution comprising 5 g/l of sodium hydroxyde (comparison support B) or etched with an acidic solution comprising 300 g/l of sulfuric acid and subsequently with an alkaline solution comprising 5 g/l of sodium hydroxyde (comparison support C) . Since the silver yield is an important parameter influencing the printing endurance of the printing plate the printing endurance can be increased by an alkaline etching by means of an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l followed by an acidic etching by means of an acidic solution comprising strong acid in a total amount of at least 150 g/l of the aluminum support.

Claims

1. A method for preparing an aluminum foil comprising the steps of roughening an aluminum foil and subsequently anodizing said aluminum foil characterized in that after the roughening and before the anodization said aluminum

foil is etched with an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l and subsequently with an acidic solution comprising strong acid in a total amount of at least 150 g/l.

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2. A method according to claim 1 wherein said alkaline solution comprises strong alkali in a total amount from 4 g/l to 50 g/l.
3. A method according to claim 1 or 2 wherein said alkaline solution has a temperature in the range from 15°C to 50°C.
- 10
4. A method according to any of claims 1 to 3 wherein said acidic solution comprises strong acid in a total amount of at least 200 g/l.
5. A method according to any of claims 1 to 4 wherein said acidic solution has a temperature in the range from 30°C to 90°C.
- 15
6. A method according to any of claims 1 to 5 wherein said anodization is carried out at a temperature in the range from 35°C to 60°C.
7. A method according to any of claims 1 to 6 wherein said aluminum foil after said anodization is posttreated with an aqueous bicarbonate containing solution.
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8. A method wherein an image receiving layer containing physical development nuclei is applied on an aluminum foil characterized in that said aluminum foil is obtained according to the method of any of the claims 1 to 7.
- 25
9. A method according to claim 8 wherein there is further applied a silver halide emulsion layer to said image receiving layer.
- 30
10. Use of a roughened and anodized aluminum foil as a support in the preparation of a mono-sheet material suitable for use according to the silver salt diffusion transfer process comprising on said aluminum foil in the order given a layer comprising physical development nuclei and a silver halide emulsion layer, characterized in that after the roughening and before the anodization said aluminum foil is etched with an alkaline solution comprising strong alkali in a total amount from 3 g/l to 75 g/l and subsequently with an acidic solution comprising strong acid in a total amount of at least 150 g/l.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2767

DOCUMENTS CONSIDERED TO BE RELEVANT							
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)				
X Y	DE-A-22 51 382 (FUJI PHOTO FILM CO LTD) * page 5, line 2 - line 11; claims; examples * * page 5, line 24 - page 6, line 6 * ---	1-9 7-10	B41N3/03				
X	US-A-3 756 826 (W.G. ZELLY) * column 2, line 45 - line 57 * ---	1-6					
X	FR-A-2 267 888 (FUJI PHOTO FILM CO LTD) * claim 10; example 15 * ---	1,7					
X	US-A-4 833 065 (H.NAKANISHI ET AL.) * column 2, line 53 - line 59; example 1 * * column 3, line 19 - line 31 * ---	1					
A	GB-A-879 767 (ALGRAPHY LIMITED) * claims * ---	1					
D,Y	EP-A-0 567 178 (AGFA-GEVAERT N.V.) * the whole document * ---	7-10					
Y	FR-A-2 284 902 (FUJI PHOTO FILM CO LTD) * page 5, line 20 * ---	7	<table border="1"> <thead> <tr> <th colspan="2">TECHNICAL FIELDS SEARCHED (Int.Cl.6)</th> </tr> </thead> <tbody> <tr> <td colspan="2">B41N</td> </tr> </tbody> </table>	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		B41N	
TECHNICAL FIELDS SEARCHED (Int.Cl.6)							
B41N							
A	FR-A-874 531 (S.A. POUR LA PROTECTION ET LA COLORATION DER MÉTAUX) * the whole document * -----						
The present search report has been drawn up for all claims							
Place of search THE HAGUE		Date of completion of the search 24 January 1996	Examiner Rasschaert, A				
<table border="0"> <tr> <td style="vertical-align: top;"> CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </td> <td style="vertical-align: top;"> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document </td> </tr> </table>				CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		
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