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PLANOGRAPHIC PRINTING PLATES

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This application is a continuation-in-part of copending application Serial No. 124,804, filed July 18, 1961, now U.S. Patent No. 3,220,832.

This invention relates to plates for planographic printing, wherein aluminum is used as a supporting material for the reproduction coating and is provided with a thin coating consisting of one or more phosphonic acids and/or derivatives thereof.

Aluminum that is to be used as supporting material for the preparation of planographic printing plates requires a preliminary treatment to enable the reproduction coating to adhere well. Virgin aluminum sheet has been processed mechanically, by means of graining machines, or steel or plastic brushes, to give a suitable supporting material. Light-sensitive coatings do not, however, adhere to material treated in this way to the extent that is desirable, if very long printing runs are to be obtained. The aluminum surface has also been first cleaned with alkaline agents, possibly then etched with nitric acid, and finally silicated by treatment with aqueous alkali silicate solutions. Aluminum treated in this way has the disadvantage that only a very few types of light-sensitive coatings, all negative-working, adhere thereto.

Aluminum has also been treated electrolytically for reproduction purposes. This process is, however, very troublesome, particularly with regard to current supply in the case of the processing of a continuous band of material, and where wide bands of aluminum are being treated.

Planographic printing plates comprising an aluminum support and a reproduction coating adherent thereto have now been found in which there is a thin intermediate layer between the aluminum support and the reproduction coating, the thin intermediate layer consisting wholly or in part of at least one phosphonic acid and/or derivative thereof.

For the preparation of the planographic printing plates of the invention, aluminum plates which have a phosphonic acid coating are coated with a reproduction coating, preferably dissolved in a solvent, by known methods, e.g., immersion, roller application, application to the support while rotating, and the like. The solvent is then removed and aluminum supports covered with an even, homogeneous coating are thereby obtained which can be converted by known methods into plates ready for printing.

The phosphonic acid coating is produced on ordinary commercial grade aluminum, particularly in the form of plates or, with continuous processing, in the form of continuous bands, in accordance with known methods for the production of coatings. The aluminum may be subjected, before the phosphonization process, to one of the known cleaning processes, e.g., in hot alkali phosphate or carbonate solution, in oxidizing agents such as dilute nitric acid, or in nitrate, chromate or hydrogen peroxide solutions. The aluminum may also be cleaned by the aid of electric current, either cathodically or anodically.

The aluminum can then be immersed in cold or hot solutions of phosphonic acids, or derivatives or substitution products thereof, in water or in inorganic or organic solvents. A phosphonic acid coating may also be formed

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by roller application or by the application of phosphonic acid solutions to the supporting material while rotating.

The phosphonic acids used in the present invention include organic phosphonic acids and derivatives thereof in the broadest possible sense, including aromatic, substituted aromatic, substituted and non-substituted saturated and unsaturated cyclic, aliphatic, heterocyclic phosphonic acids and also polymers and interpolymers of unsaturated phosphonic acids with each other or with other vinyl compounds, as well as derivatives thereof, such as salts or esters.

The following may be mentioned by way of example: vinyl phosphonic acid, polyvinyl phosphonic acid, 2-phosphono-ethane-1-sulfonic acid, vinyl phosphonic acid mono-methyl ester, vinyl phosphonic acid ethyl ester, 4-chlorophenyl phosphonic acid, 4-chloro-3-nitrophenyl phosphonic acid, 5 nitronaphthalene phosphonic acid, β -styryl phosphonic acid and interpolymers of vinyl phosphonic acid with acrylic acid and vinyl acetate or mixtures thereof and their salts. Depending upon the nature of the aluminum surface, the temperature employed and the concentration of the phosphonic acid solution, the treatment requires from a few seconds to several minutes. In general, treatments of 5 seconds to 10 minutes, preferably 60 seconds to 2 minutes, at temperatures of 20-100° C. with about 0.001 to 10% (preferably 0.01-3%) solutions of phosphonic acids are adequate. The treatment may be further prolonged and either higher or lower concentrations may be used if desired. However, conditions outside the range mentioned may often either be less favorable or not produce any improvement in results. If the aluminum plates are immersed in a bath, the bath may contain 0.1% phosphonic acid solutions in water or organic solvents, for example; if the coating is to be applied to the support, while rotating, 0.01-1% phosphonic acid solutions in organic solvents such as methyl ethyl ketone, toluene, butyl acetate, ethylene glycol monomethyl ether or dimethyl formamide or mixtures thereof are preferably used.

Suitable compounds to improve the hydrophilic properties of the aluminum surface, such as hydrophilic colloids, e.g., cellulose ethers such as carboxymethyl cellulose, hydroxyethyl cellulose and methyl cellulose or alginates, may be added to the phosphonic acid solutions.

The resultant phosphonic acid coating may be briefly rinsed with water and then dried. Drying at fairly high temperatures has an advantageous effect on the adhesion of the coatings. Solutions of the organic reproduction coatings can then be coated by hand or by means of suitable coating machines.

The materials used for the reproduction coatings for the planographic printing plates of the present invention are, in general, any with which, as a result of the action of visible, ultra-violet or infra-red light or X-rays or heated objects, image-wise differentiation is possible, e.g. light-sensitive organic compounds such as aliphatic and aromatic esters, hydrazides and amides of naphthoquinone-diazide sulfonic acids, cinnamal malonic acid, its substitution products and functional derivatives, diazonium salts of amino-diphenylamine and condensation products thereof with formaldehyde, ortho and para-quinone diazides of benzene, anthracene and heterocyclic systems, e.g. of quinoline, indazole, benzimidazole, fluorene and diphenylene oxide, also diazo ketones, unsaturated ketones, ortho and para-iminoquinone diazides, derivatives of alkyl-nitrophenylene sulphonic acids, nitroaldehydes, acenaphthenes, nitrons, stilbenes, azides and diazides and higher-polymeric diazo compounds.

A particularly suitable light-sensitive substance is a condensation product free of metal salts and obtained by

acid condensation of a diphenylamine-4-diazonium salt with formaldehyde. When a light-sensitive substance of this kind is employed, the copying material is highly light-sensitive, has very good shelf-life, and is very resistant to rubbing.

Examples of suitable polyfunctional diazonium salts free of metal salts are those obtained by condensation of the diazonium salt, e.g. diphenylamine-4-diazonium chloride, diphenylamine-4-diazonium bromide, or diphenylamine-4-diazonium phosphate, with formaldehyde in strong phosphoric acid or polyphosphoric acid. The crude condensate may be diluted and then applied direct to aluminum which has been pretreated with a phosphonic acid and dried. However, after the completion of condensation, the phosphoric acid may be separated from the reaction mixture in the form of a feebly soluble salt by treatment with a suitable metal carbonate, bicarbonate or hydroxide, and the readily soluble neutral halide of the condensation product may be isolated in solid form by evaporation. It is not essential for phosphoric acid to be used as condensation agent; the condensation product can also be obtained by condensation of an unsubstituted or substituted diphenylamine-4-diazonium halide with formaldehyde in hydrofluoric acid, hydrochloric acid or hydrobromic acid and recovering the condensation product by evaporation in vacuo.

Also, reproduction coatings can be applied which have a high electrical resistance in the absence of light but which decreases by several powers of ten under the influence of light or heat, such as are used in electrophotography and electrothermography, e.g. organic photoconductors of lower or high molecular weight, if desired in association with resins. Photoconductors that have proved particularly suitable are oxadiazoles, imidazolones, triazoles, oxazoles, thiazoles, hydrazones, triazines, polyvinyl carbazoles and polyvinyl oxazoles.

As the resins, those which are suitable have groups conferring alkali-solubility such as acid anhydride, carboxylic acid, sulfonic acid, sulfonamide or sulfonimide groups, e.g., vinyl polymers and vinyl interpolymers, phthalic acid ester resins, maleinate resins, alkyd resins, colophony resins and polyacrylic acid resins.

The planographic printing plates of the invention have the advantage that practically all known types of reproduction coatings adhere excellently to the phosphonic acid surface and, moreover, after the usual image-wise exposure and removal of the coating in the image-free parts (which may be effected with water, weak alkalis or acids, according to the type of reproduction coating used), they give long printing runs in the machines normally used for offset printing, sometimes several times the length of those obtained with grained aluminum foils such as have hitherto been used. The planographic printing plates have the further advantage that they are very easy to prepare, as ordinary rolled aluminum sheet can generally be passed immediately to a bath and subjected to the phosphonic acid treatment.

The invention will be further illustrated by reference to the following specific examples:

Example 1

A mechanically roughened aluminum foil is immersed for 60 seconds at 20° C. in a bath containing 0.01 percent by weight of polyvinyl phosphonic acid in pure water and dried. Thereafter, one surface of the foil is coated with a solution consisting of 1 part by weight of 4-dimethylamino-benzaldehyde-phenyl-hydrazone, 0.8 part by weight of phthalic acid ester resin free of fatty acid and having a softening point of 75 to 90° C. (method of Kraemer, Sarnow, Nagel) and an acid value of 85 to 100, and 30 parts by weight of glycol monomethyl ether. The dried coating adheres firmly to the foil and is useful for electrophotographic processes.

For making a printing plate, the coating is charged by a corona discharge and then exposed under a master

for one second to a 125 watt mercury lamp, whereupon it is powdered over with an electrophotographic developer comprising a powdered resin having a melting range below 100° C. and containing melted-in carbon black. After removal of the powder from those areas of the foil where no electrostatic forces make it adhere to the foil, i.e. from the areas which have been exposed to light, the foil is heated for a few seconds to a temperature of 150° C., whereupon the coated surface carries an image of melted powder which corresponds to the image used as the master in the exposure step. The imaged surface of the foil is wiped over with an aqueous solution containing 5 percent by weight of morpholine, 5 percent by weight of sodium silicate, and 3 percent by weight of carboxy methyl cellulose. After rinsing with water and inking up with greasy ink, a printing plate ready for making prints is obtained.

Example 2

A thin band of virgin aluminum sheet is drawn through a bath containing a hot (80° C.) solution of 0.1 percent by weight of vinyl phosphonic acid and 0.01 percent by weight of carboxy methyl cellulose in water. The band is then dried and coated with a solution composed of 1 part by weight of poly-[2-vinyl-4-(4'-dipropyl-amino-phenyl)-5-(2'-chlorophenyl)-oxazole], 0.8 part by weight of a styrene-maleic anhydride interpolymer having a specific gravity of 1.15 and a decomposition temperature of 200° C., and 30 parts by weight of glycol monomethyl ether. After drying the coating, an electrophotographic printing material is obtained which is distinguished by a firm adherence of the electrophotographic coating to the aluminum base.

For conversion into a printing plate, the material is exposed, developed and fixed as described in the foregoing Example 1, and then treated with a dilute (0.1%) aqueous sodium hydroxide solution which is rubbed in. Thereafter, it is rinsed down with water, treated with dilute (3%) phosphoric acid, and inked up with greasy ink.

Example 3

An aluminum foil is coated on a rotating disc with a 1 percent solution of 5-nitronaphthalene phosphonic acid in glycol monomethylether, dried, and then coated with a solution composed of 1 part by weight of 2,5-bis-(4'-diethylaminophenyl)-1,3,4-triazole, 0.8 part by weight of a colophony ester resin having a softening range of 110° to 115° C. and an acid number in the range of 210 to 240, and 30 parts by weight of glycol monomethylether; and dried.

The thus prepared material was used for making a printing plate by providing the coated surface of the foil with an image of melted powder as described in Example 1 above, treating the imaged surface of the foil with a solution consisting of 1 part by weight of ammonia solution (25% b.w.) and 9 parts by weight of polyethylene glycol, rinsing down with water, rubbing in with dilute phosphoric acid, and inking up with greasy ink.

Example 4

An aluminum foil is coated on a plate whirler with a solution of 0.05 percent by weight of vinyl phosphonic acid and 0.05 percent by weight of polyvinyl phosphonic acid in ethyleneglycol monomethylether, dried, and coated with a solution containing, in 30 parts by weight of ethyleneglycol monomethylether, 0.8 part by weight of a maleic resin having a softening range of 120 to 130° C. and an acid number between 110 and 130, and 1 part by weight of a mixture consisting of equal parts by weight of 3-(4'-dimethylaminophenyl) - 5 - (4''-methoxyphenyl)-6-phenyl-1,2,4-triazine and 3-(4'-dimethylaminophenyl) - 5-phenyl - 6 - (4''-methoxyphenyl)-1,2,4-triazine. After evaporation of the solvent, the coating adheres firmly to the aluminum foil.

The thus obtained material was converted into a printing plate as described in Example 1, with the exception

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that for making the non-image areas of the imaged surface hydrophilic, it was treated with a 10 percent by weight solution of ethanalamine in polyethylene glycol containing 3 percent by weight of sodium silicate.

Example 5

A mechanically roughened aluminum foil is immersed for 5 minutes at 70° C. in a 20 percent aqueous solution of trisodium phosphate and then for 60 seconds at 20° C. in a bath of 0.1 percent aqueous polyvinyl phosphonic acid. After this layer has been dried, it is coated with a solution, in 30 parts by weight of ethyleneglycol monomethylether, of 1 part by weight of 1,3,5-triphenylpyrazole, 0.8 part by weight of a styrene-maleic anhydride interpolymer containing carboxyl groups and having a specific weight of 1.15 and a decomposition temperature of 210° C., and 0.003 part by weight of Ethyl Violet, and dried.

The conversion of the thus obtained electrophotographic material into a printing plate is performed as described in Example 1, with the sole exception that the non-image areas were rendered more hydrophilic by a treatment of the plate with a solution of 10 parts by weight of triethanol amine, 30 parts by weight of ethyleneglycol, and 60 parts by weight of glycerin.

Example 6

One part by weight of 2,5-bis-[4'-diethylaminophenyl-(1')]-1,3,4-oxadiazole, 0.8 part by weight of a styrene-maleic anhydride interpolymer containing carboxyl groups and having a specific gravity of 1.26 to 1.28 and a decomposition temperature ranging from 200 to 240° C., and 0.003 part by weight of Rhodamine B extra (Schultz: "Farbstofftabellen," 7th edition, vol. 1, No. 864) are dissolved in 30 parts by weight of ethyleneglycol monomethyl ether. The solution is coated upon an aluminum foil which has been treated for the production of a phosphonic acid coating as described in Example 1, and then dried. For the production of images on the electrophotographic material thus prepared, the coating is charged by means of a corona discharge and then exposed under a master for one second to a 125 watt mercury lamp. The resultant electrostatic image of the master is made visible by dusting over with a resin powder pigmented with carbon black and fixed as an irremovable electrocopy by heating to 150° C. For the preparation of a printing plate, the electrocopy is wiped over with a solution consisting of 30 parts by volume of methanol, 20 parts by volume of glycerine, and 35 parts by volume of ethylene glycol monomethyl ether. The plate is then briefly rinsed with water and treated with dilute (about 0.5 to 5%) aqueous phosphoric acid solution. After the resulting printing plate has been inked up with greasy ink, it can be used for printing in the usual manner in an offset machine, direct images corresponding to the master being obtained.

Example 7

A mechanically roughened aluminum foil is immersed for 60 seconds at 30° C. in a solution in water of 0.8 percent of polyvinyl phosphonic acid and 0.2 percent of vinyl phosphonic acid. After the aluminum foil has been rinsed with water and dried, the foil is coated with a solution consisting of 1 part by weight of 2-(4-diethyl-

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aminophenyl)-4,5-diphenyl-imidazole, 0.8 part by weight of a styrene-maleic anhydride interpolymer having a decomposition temperature in the range of 200 to 240° C. and a specific weight of 1.26 to 1.28, 0.001 part by weight of Rhodamine B extra, and 30 parts by weight of ethyleneglycol monomethyl ether, and the coating is dried.

The thus obtained material was converted into a printing plate by the application thereto of a melted-on image as described in Example 1, and treating the thus imaged surface of the foil with a solution consisting of 5 percent of ethanol amine, 5 percent of diethanol amine, 10 percent of methyl alcohol, 55 percent of ethylene glycol, 20 percent of glycerin, and 5 percent of sodium silicate.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. An electrophotographic material comprising an aluminum base, a first layer on the base comprising at least one compound selected from the group consisting of an organic phosphonic acid and the esters and salts thereof, and a second layer on the first layer, the second layer being a photoconductive layer.

2. An electrophotographic material according to claim 1 in which the first layer comprises polyvinyl phosphonic acid.

3. An electrophotographic material according to claim 1 in which the first layer comprises vinyl phosphonic acid.

4. An electrophotographic material according to claim 1 in which the first layer comprises 5-nitronaphthalene phosphonic acid.

5. An electrophotographic material according to claim 1 in which the second layer comprises a mixture of an oxadiazole and a styrene interpolymer containing carboxyl groups.

6. A photographic reproduction process which comprises exposing an electrostatically charged photoconductive insulating layer to light under a master and developing the resulting image with an electroscopic material, the photoconductive layer being supported on an intermediate layer comprising at least one compound selected from the group consisting of an organic phosphonic acid and the esters and salts thereof, and the intermediate layer being supported on an aluminum base.

7. A photographic reproduction process according to claim 6 in which the intermediate layer comprises polyvinyl phosphonic acid.

8. A photographic reproduction process according to claim 6 in which the intermediate layer comprises vinyl phosphonic acid.

9. A photographic reproduction process according to claim 6 in which the intermediate layer comprises 5-nitronaphthalene phosphonic acid.

10. A photographic reproduction process according to claim 6 in which the photoconductive layer comprises a mixture of an oxadiazole and a styrene interpolymer containing carboxyl groups.

No references cited.

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