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PROCESS FOR THE PREPARATION OF A PRINTING PLATE MADE FROM A DIAZONIUM SALT MIXED WITH AN ORGANIC ACID FROM THE GROUP CONSISTING OF PHOSPHONIC, PHOSPHINIC AND ARSONIC ACIDS

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22 Claims. (Cl. 96—33)

Co-pending application Ser. No. 429,625 which corresponds to German Patents Nos. 1,134,093 and 1,160,733, relates to a presensitized planographic printing plate with good adhesion of the reproduction coating, in which aluminum is used as support material for the reproduction coating, the aluminum being provided with a thin coating of one or more phosphonic acids or derivatives thereof. In one embodiment of the printing plates of the co-pending application, the reproduction coating adhering to the coating of phosphonic acid or derivative thereof contains as a light-sensitive substance a condensation product of a salt of a diphenylamine-4-diazonium compound with formaldehyde; the condensation product is free from metal salts and is prepared in acid medium. The use of polyvinylphosphonic acid for the preparation of presensitized printing plates is described in U.S. Patent No. 3,179,518, in which there is disclosed the application to a supporting foil of a light-sensitive solution which contains, in addition to a diazo compound, small amounts of polyvinylphosphonic acid. The process described in the cited U.S. patent has the advantage that the foil serving as a support need be coated with one solution only. However, this known process, because of the only limited compatibility of diazonium compounds and polyvinylphosphonic acid with each other in the solution, renders possible only the application of solutions in which the content of polyvinylphosphonic acid is moderate. Consequently, this process leads in some cases to only a moderate improvement in the service life of a printing plate prepared with polyvinylphosphonic acid in the coating solution. Further, the coating solution used in the known process is very sensitive to comparatively slight changes in the environment. For example, in the case of a lowering of the temperature, or a subsequent change in the coating solution by increasing one or more of the dissolved constituents thereof, the result can be turbidity or precipitation in the solution. Turbidities or precipitations in the solution, however, often result in inferior printing foils, so that where turbidities or precipitations occur, clarification of the solution, generally by filtration, is performed.

It has now been found that, in order to avoid the aforementioned disadvantages in the preparation of a presensitized printing plate, which preparation is effected by application of a solution, which contains a light-sensitive diazonium salt and an organic acid as an adhesion agent, to a metallic support and drying the applied coating, it is of great advantage to apply a solution which contains, together with the diazonium salt, at least one organic acid, acting as an adhesion agent, and selected from the group consisting of phosphonic acids, phosphinic acids and arsonic acids, with the exception of polyvinylphosphonic acids.

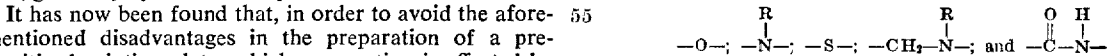
By the use of the coating solutions, which according to the invention contain, together with diazonium salt, a phosphonic acid other than polyvinylphosphonic acid, preferably a phosphonic acid of low molecular weight, or phosphinic acid or arsonic acid, there are avoided the disadvantages to which the use of polyvinylphosphonic

acid is subject by reason of turbidities and precipitation occurring in the coating solutions. It has been found that the organic acids used according to the present invention yield, either with water or organic solvents, or a mixture of both, clear coating solutions which are ready to be used for coating. One embodiment of the process consists, e.g., in adding to an aqueous solution of a diazonium salt, a phosphonic acid which precipitates the diazonium salt out of the aqueous solution (not all of the phosphonic acids which are efficacious within the scope of this invention yield precipitates). The precipitated diazonium salt is separated from the phosphonic acid and, when dissolved in an organic solvent, used for coating.

As soon as the phosphonic acids, phosphinic acids and/or arsonic acids are incorporated in the reproduction coatings, and also when diazo compounds of low molecular weight are used whose light decomposition products, without additives, do not adhere or adhere only very poorly to the coating support, it is possible to obtain printing plates from which a large number of flawless prints can be made. The development of presensitized reproduction material prepared according to the invention, and exposed in conventional manner under a transparent negative, can be effected with water, aqueous solutions of phosphoric acid, or aqueous solutions of alkali salts of phosphoric acid, depending on which phosphonic acid or arsonic acid is used. Positive printing plates are obtained.

Planographic printing plates prepared according to the present invention have the advantage that the coating support can, without chemical pretreatment, be sensitized with the coating solutions of the invention, whereas, in the case of the heretofore known planographic printing plates chemical pretreatment of the coating support must be effected in a separate operation before application of the light-sensitive coating solution. As a coating support for use in the process of the invention, aluminum is suitable. Preferably, aluminum foils are used the surface of which has been finely roughened by metal brushes. However, aluminum foils which have been chemically pretreated, anodized or covered with a coating of boehmite also may be used, but such pretreatment is not necessary when the process according to the invention is used. It may, however, be advantageous to clean the aluminum foil before sensitizing is effected. Cleaning may be effected, for example, by treatment with an alkali phosphate solution, followed by washing with nitric acid and water.

Diazo compounds which may be used in this invention are, particularly, those diazonium salts which contain at least 2 phenyl nuclei which may be linked to each other directly or via intermediate groups, e.g.



(*R*=*H*, alkyl, aryl, aralkyl, or acyl).

The phenyl nuclei may have substituents as well. The compounds also may be used in the form of condensates with aldehydes or ketones.

However, other diazo compounds, for example those which are derived from p-phenylenediamine but contain only one phenyl nucleus, also may be used. An example is the diazo compound derived from 4-amino-2,5-dibutoxyphenylmorpholine. A number of diazo compounds suitable for the process of the invention are listed in U.S. Patents Nos. 3,062,644, and 3,061,429. The compounds are used in the patented processes together with polyacrylic acid or a polycarboxylic acid of similar structure. A disadvantage of this reproduction material, compared with that of the present invention, is the very low resist-

ance to acid of printing plates prepared from the former. Since, however, it is usual to wipe over offset plates which tend to tone with phosphoric acid, the wiping over being effected in order to make them hydrophilic again, it is very desirable to prepare printing plates which are more resistant to acid. The printing plates prepared according to the process of the present invention possess this increased acid-resistance, as can be seen from the use of strong phosphoric acid as developer in many cases.

The diazo compounds may be present in the form of salts of inorganic acids as well as in the form of double salts of metal halides, for example with zinc chloride. It is particularly favorable to use the diazonium salts in the form of chlorides.

The concentration of the diazo compound in the coating solution generally is between 0.01% and 10% by weight, preferably between 0.2 and 5% by weight. As solvents, e.g. the methyl and ethyl ethers of ethyleneglycol, dioxane, dimethylformamide, diacetone alcohol, lower aliphatic alcohols or ketones, water, and mixtures of organic solvents with water, are suitable.

In the process of the invention, very different groups of phosphonic acids, phosphinic acids and arsonic acids, such as, e.g. aliphatic, aromatic and heterocyclic phosphonic acids, are suitable. The following are exemplary:

chloromethanephosphonic acid
arsonacetic acid
butane-1-arsonic acid
benzenephosphonic acid
benzenearsonic acid
benzylarsonic acid
4-hydroxy-phenylarsonic acid
4-nitrophenylarsonic acid
4-hydroxy-3-nitro-phenylarsonic acid
phenoxymethylphosphonic acid
4-methylphenoxymethylphosphonic acid
3-methylphenoxymethylphosphonic acid
4-chlorophenoxymethylphosphonic acid
naphthalene-2-phosphonic acid
naphthalene-1-arsonic acid
5-nitronaphthalene-1-phosphonic acid
diphenylphosphinic acid
4-dimethylaminophenylazo-benzene-4'-arsonic acid.

The phosphonic, phosphinic or arsonic acids are incorporated into the reproduction coating in an amount of 0.05 to 3 moles, preferably 0.2 to 1.5 moles per mole of diazo groups; by 1 mole of acid is meant that weight which corresponds to 1 gram atom of phosphorus or arsenic, respectively.

In practicing the process, at least one diazonium salt and at least one phosphonic, phosphinic or arsonic acid is dissolved in a solvent. Dyes, wetting agents, resins and other additives useful in diazo coatings also may be added to these solutions. Coating of the support with the coating solution containing the diazo compound and phosphonic or arsonic acid may be effected in the usual manner, e.g. by application by hand, using a pad of cotton, by immersion, by whirl-coating or by application by means of rollers. Drying preferably is effected in a moderately warm air stream.

Development of the plate, exposed under a negative, generally can be effected by wiping over with dilute aqueous phosphoric acid; positive printing plates are obtained. In many cases, inking up can be effected with the same pad of cotton, still moist with acid, without adverse effects on the printing plate. It may be advisable, after inking up, to clean the printing plate again by wiping over with dilute phosphoric acid. When there is an appreciable lapse of time between coating and processing of the reproduction material, it may be necessary to increase the acid concentration in the developer or to lengthen the time of developing. Details of the developers to be used and of the developing methods are given in the following examples which further illustrate the process.

In the examples, parts by weight bear the same relation to parts by volume as grams to ml. Where percentages are stated, they are percent by weight.

Example 1

An aluminum support roughened by brushing, is coated on a whirl-coater with a solution containing 1 part by weight of diphenylamine-4-diazonium chloride (93.3%) and 0.05 part by weight of 4-methylphenoxymethylphosphonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and dried in a warm air stream.

When preparing the printing plate, after exposure under a negative original, development is effected by wiping over with aqueous 10% phosphoric acid, and inking up with protective ink. A positive printing plate is obtained which is cleaned with approximately 2% aqueous phosphoric acid and then gummed. The printing plate permits the making of numerous flawless copies on a conventional offset machine.

If preparation of the light-sensitive plate is effected with the above solution, but omitting the phosphonic acid, a material is obtained whose reproduction coating, after exposure, adheres only poorly to the coating support, so that it is damaged by mere wiping over with water and is even completely removed by treatment with 1.4% aqueous phosphoric acid.

This difference between a reproduction coating which contains no phosphonic acid and a reproduction coating which does contain phosphonic acid remains when there are used for the coatings the coating solutions described above diluted five times with ethyleneglycolmonomethylether. The plate containing phosphonic acid can in this case be developed by brief wiping over with 1.4% aqueous phosphoric acid. After subsequent rinsing with water, the light decomposition products accept greasy ink well. A plate prepared in an analogous manner, but without phosphonic acid in the coating solution, is severely damaged when the same method of development is followed.

Example 2

An aluminum foil, roughened by brushing is coated by applying thereto, with a pad of cotton, a solution of 1 part by weight of diphenylamine-4-diazonium chloride and 0.5 part by weight of 3-methyl-phenoxymethylphosphonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and dried in a warm air stream.

When processing into a printing plate, the same procedure is followed as in Example 1.

Example 3

An aluminum support, roughened by brushing, is coated with a solution of 1 part by weight of diphenylamine-4-diazonium chloride (93.3%) and 0.5 part by weight of phenylphosphonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and the plate is dried in a warm air stream.

The reproduction material obtained, after exposure under a negative, is developed with 10 to 20% aqueous phosphoric acid and then inked up, using the same pad of cotton. The plate is then washed with water and gummed. The printing run achieved with the thus prepared printing plate is excellent.

Example 4

An aluminum support, roughened by brushing, is coated with a solution which contains 1 part by weight of diphenylamine-4-diazonium chloride (93.3%) and 0.412 part by weight of chloromethylphosphonic acid in 100 parts by volume of ethyleneglycolomonomethylether, and then dried in a warm air stream.

The presensitized printing plate thus prepared is exposed under a negative original, and developed with 1.4% aqueous phosphoric acid. After the plate has been washed with water, it is inked up with protective ink in conventional manner.

A positive printing plate is obtained.

Example 5

An aluminum support, roughened by brushing, is coated, using a pad of cotton, with a coating solution containing 0.5 part by weight of 4-methoxy-diphenylamine-4'-diazonium chloride and 0.5 part by weight of a polyfunctional phosphonic acid (the preparation of which is described below) in a mixture of 50 parts by volume of dimethylformamide and 50 parts by volume of water. The plate is dried in a warm air stream.

Development of the plate after it has been exposed under a negative original can be effected by wiping over with 20% aqueous phosphoric acid, using a pad of cotton, and the printing plate then can be inked up with the same pad of cotton and, if necessary, wiped over with the developer in order to clean it.

A positive printing plate is obtained.

If the phosphonic acid is omitted from the sensitizing solution, but otherwise the same procedure followed as that stated above, the light-decomposition products do not adhere sufficiently to the support; they are removed to a large extent merely by wiping over with 1% aqueous phosphoric acid and subsequent inking up.

The phosphonic acid employed is prepared as follows: 3.8 parts by weight of phenoxymethylphosphonic acid are dissolved in 6 parts by volume of water. 2.5 parts by weight of a 30% aqueous solution of formaldehyde are added and the mixture is boiled under reflux for 20 minutes. The reflux condenser is then removed and the mixture is heated to 110° C. for 1 hour. There remains a viscous mass which, during cooling, solidifies in vitreous form and forms a clear solution in water. This product is the polyfunctional phosphonic acid used in this example.

Example 6

An aluminum support, roughened by brushing, is coated with a coating solution consisting of 0.4 part by weight of a chloride (90.5%) of the condensation product described in Example 5 of German Patent No. 1,138,399, (obtained from 3 - methoxy-diphenylamine-4-diazonium chloride and formaldehyde by condensation in 85% phosphoric acid), 0.264 part by weight of naphthalene-2-phosphonic acid, 8 parts by volume of water and 92 parts by volume of a mixture consisting of 60 parts by volume of ethyleneglycolmonomethylether and 40 parts by volume of dimethylformamide.

Processing of the presensitized printing plate thus obtained into a printing plate is carried out as in Example 5.

Example 7

An aluminum support, roughened by brushing, is coated with a solution of 1.05 parts by weight of N-ethyl-benzylaminobenzene-4-diazonium chloride zinc chloride salt (95%) and 0.46 part by weight of benzenephosphonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and dried in a warm air stream.

Development of the plate, after it has been exposed under an original, is effected with a 7% aqueous solution of gum arabic. The printing plate is then inked up with greasy printing ink.

Before inking up, the printing plate may be reinforced with a lacquer. Suitable for the lacquer reinforcement is e.g. the lacquer disclosed in Example 1 of Belgian Patent No. 623,787.

If the aforementioned diazonium salt solution is used without the addition of phosphonic acid and is applied to an identical coating support, the image is completely destroyed merely by development of the exposed plate with water and subsequent inking up with protective ink.

Example 8

An aluminum support, roughened by brushing, is coated with a solution which contains 1 part by weight of diphenylamine-4-diazonium chloride (93.3%) and 0.5 part by weight of 4-hydroxyphenylarsonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and dried by being left to stand in the air. To complete the drying, it is further dried for 2 minutes at 100° C. in a drying cabinet.

Development of the presensitized printing plate thus obtained is effected, after exposure under an original, with water or 1% phosphoric acid.

Example 9

An aluminum support, roughened by brushing, is coated on a whirl-coater with a solution containing 0.48 part by weight of 2,5-4'-triethoxydiphenyl-4-diazonium bromide and 0.155 part by weight of 5-nitronaphthalene-1-phosphonic acid dissolved in 50 parts by volume of ethyleneglycolmonomethylether, and dried in a warm air stream.

After exposure under a negative original of the thus obtained light-sensitive material, a positive printing plate is obtained by development with 10 to 20% aqueous phosphoric acid and inking up while the surface is still moist with the developer.

If an identical support is sensitized in the same manner, but omitting the phosphonic acid, a reproduction material is obtained whose light decomposition products are completely removed from the support merely by development with 0.2% aqueous phosphoric acid.

Example 10

An aluminum support, roughened by brushing, is coated with a coating solution containing 1 part by weight of the diazonium salt crude condensate described below and 0.39 part by weight of 1-nitrobenzene-4-arsonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and then dried with warm air.

After exposure under a negative original, development of the thus obtained presensitized reproduction material into a positive printing plate can be effected by wiping over with 10 to 20% aqueous phosphoric acid. A reproduction material prepared in the same manner, but without the arsonic acid, yields printing plates which under the action of dilute aqueous phosphoric acid become "blind" much more rapidly.

To prepare the diazonium salt crude condensate, a mixture of 24.9 parts by weight of diphenylamine-4-diazonium chloride (93.3%) and 3 parts by weight of paraformaldehyde is introduced into 29.6 parts by weight of 36.5% aqueous hydrochloric acid and condensation is effected for 7 hours at 50° C.

Example 11

An aluminum support, roughened by brushing, is coated with a solution of 1 part by weight of 4-methoxy-diphenylamine-4'-diazonium chloride and 0.2 part by weight of naphthalene-1-arsonic acid in 100 parts by volume of ethyleneglycolmonomethylether, and then dried in a warm air stream.

To prepare a printing plate, the reproduction material thus obtained is exposed under an original, developed by wiping over with dilute aqueous phosphoric acid (1–2% by weight), and, after inking up with greasy ink, can be used as a printing plate.

The properties of a plate which was rendered light-sensitive in the same manner with a solution of the same diazonium salt, but from which solution the arsonic acid was omitted, is given in Example 5.

Example 12

An aluminum foil, roughened by brushing, is coated with a solution of 1 part by weight of carbazole-3-diazonium chloride and 0.33 part by weight of benzenephosphonic acid in 100 parts by volume of ethyleneglycolmonomethylether and the solution applied is dried in a warm air stream. The printing foil, after exposure under an original, can be developed into a printing plate by wiping over with an approximately 10% aqueous phosphoric acid solution.

A printing plate prepared by the same method and using the same diazo compound, but without the phosphonic acid, exhibits a poorer resistance to phosphoric acid.

Example 13

An aluminum support, roughened by brushing, is coated with a solution containing 3 parts by weight of the diazonium compound derived from 4-amino-2,5-dimethoxy-4'-methyldiphenylsulfide (chloride as zinc chloride double salt), and 0.52 part by weight of naphthalene-2-phosphonic acid in 100 parts by volume of dimethylformamide. Drying is effected in a warm air stream. The foil, after exposure under an original, can be developed into a printing plate by wiping over with 5 to 10% aqueous phosphoric acid.

The light-decomposition products of a reproduction coating prepared in the same manner, but without the phosphonic acid, are removed merely by wiping over with water or 1 to 2% phosphoric acid.

Example 14

The same procedure is followed as in Example 13, but using as a support an electrolytically roughened aluminum foil. Again, development can be effected with 2 to 10% phosphoric acid.

Example 15

An aluminum support, roughened by brushing, is coated, using a pad of cotton, with a solution containing 1 part by weight of 1,4-dibutoxy-2-morpholino-benzene-5-diazonium chloride (zinc chloride double salt) and 0.5 part by weight of 5-nitronaphthalene-1-phosphonic acid in a mixture of 25 parts by volume of dimethylformamide and 12.5 parts by volume of water.

Development of the foil into a printing plate, after exposure under an original, can be effected by wiping over with 10% aqueous phosphoric acid.

If the same support is made light-sensitive with the above solution, but omitting the phosphonic acid, a reproduction material is obtained whose light-decomposition products are substantially removed from the support by water or 1 to 2% phosphoric acid.

Example 16

An aluminum foil, roughened by brushing, is coated with a solution of 1 part by weight of 4-methoxydiphenylamine-4'-diazonium chloride and 0.8 part by weight of diphenylphosphinic acid $(C_6H_5)_2$=POOH, in 100 parts by volume of ethyleneglycolmonomethylether. Drying is effected in a warm air stream.

The properties of the reproduction material without phosphinic acid are given in Example 5.

Example 17

An aluminum support roughened by brushing is coated with a solution of the following composition, and dried in a warm air stream.

The solution contains: 0.5 part by weight of 1,4-diethoxy-2-benzoylaminobenzene - 5 - diazonium chloride (zinc chloride double salt) (97.5%), 0.2 part by weight of polyvinylbutyral, 0.2 part by weight of benzylarsonic acid, 4 parts by volume of water, and 46 parts by volume of a mixture of 60 parts by volume of ethyleneglycolmonomethylether and 40 parts by volume of dimethylformamide.

Development of the plate, after exposure under a negative original, can be effected with 10 to 20% aqueous phosphoric acid. The printing plate then can be washed with water, inked up and, if necessary, cleaned with dilute phosphoric acid.

A reproduction material prepared in the same manner, but without the arsonic acid, yields light-decomposition products which are severely damaged merely by water, but particularly so when inking up with greasy ink is effected. The image is even more sensitive to dilute phosphoric acid. Even when the latter is greatly diluted, the image is rapidly destroyed thereby.

Example 18

A condensation product prepared by condensing 3-methoxydiphenylamine-4-diazonium chloride and formaldehyde in 85% phosphoric acid is precipitated from an aqueous solution of the condensation product by naphthalene-2-phosphonic acid, and 0.5 part by weight of the precipitated product is dissolved in a mixture of 20 parts by volume of dimethylformamide and 80 parts by volume of ethyleneglycolmonomethylether. An aluminum foil, roughened by brushing, is coated with this solution and, after initial drying, it is further dried for two minutes at 100° C. In this condition the plate can be stored for months without becoming unusable.

To prepare the printing plate, the reproduction material is exposed under a negative original and developed by wiping over with 10% aqueous phosphoric acid. When inking up is effected with a pad of cotton soaked with 10% phosphoric acid, an excellent positive printing plate is obtained.

To prepare the precipitation product, 10 parts by weight of naphthalene-2-phosphonic acid are dissolved in an equivalent amount of an aqueous solution of sodium bicarbonate (700 parts by volume of solution), and this solution is poured into a solution of 29.1 parts by weight of the aforementioned diazo condensate (used as crude condensate, i.e. with the inclusion of the phosphoric acid used as a condensation medium) in a mixture of 200 parts by volume of water and 200 parts by volume of a saturated aqueous solution of sodium acetate. A clear solution results which is acidified at a pH of 3 by adding dilute aqueous hydrochloric acid; the precipitation produce precipitates as a viscous mass. After standing for about a day, the mother liquor is decanted and the still viscous precipitation product is washed with water and dried in the air. After standing for several days in the air, the product solidifies and can be pulverized. According to analysis, the precipitation product contains 1.5 molecules of naphthalene-2-phosphonic acid per diazo group. Similar good results are obtained when, in order to prepare the reproduction material, an identical aluminum support is coated, by application with a pad of cotton, with a 2% solution (in dimethylformamide) of a precipitation product which is prepared in an analogous manner from the same diazo compound and 4-nitronaphthalene-1-phosphonic acid.

Example 19

An aluminum foil, roughened by brushing, is coated with a coating solution which contains 0.2 part by weight of a precipitation product, described below, in a mixture of 4 parts by volume of water and 96 parts by volume of ethyleneglycolmonomethylether. The thus coated foil is dried with a warm air stream. It can be exposed under an original in conventional manner and converted into a printing plate, e.g. by development with 10 to 20% aqueous phosphoric acid and inking up with greasy ink.

To prepare the precipitation product, 2.48 parts by weight of diphenylamine-4-diazonium chloride (93%) are dissolved in 30 parts by volume of water and a warm solution of 2.02 parts by weight of 4-methylphenoxymethylphosphonic acid in 40 parts by volume of water is added. An oily precipitate is immediately formed which crystallizes completely after a short time. After cooling, it is filtered with suction, washed with ice water, then with ether, and dried. The precipitation product is free from chlorine and, according to analysis, contains one phosphonic acid group for each diazo group.

Example 20

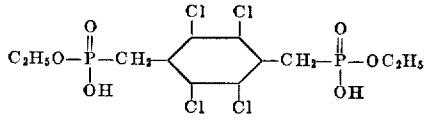
An aluminum foil, roughened by brushing, is coated with a solution prepared as follows: 0.26 part by weight of the chloride of a condensation product prepared from

4-methyldiphenylamine-4'-diazonium sulfate and formaldehyde by condensation in 78% sulfuric acid (the condensation product being obtained in the form of the chloride by the method of Example 4 of German Patent No. 1,138,400) is dissolved in 10 parts by volume of water, and a solution of 0.224 part by weight of 4-chlorophenoxymethylphosphonic acid in 15 parts by volume of water is added. A viscous precipitate forms immediately and deposits on the walls of the vessel. As soon as it is completely deposited, the aqueous phase is decanted, washing is effected with a little water and the precipitate is dissolved in a mixture consisting of 40 parts by volume of ethyleneglycolmonomethylether and 10 parts by volume of butyl acetate.

The brushed aluminum foil is coated with this solution, e.g. on a whirl-coater, and then dried with a warm air stream. After exposure under a transparent negative original, developing is effected by wiping over with 20% aqueous phosphoric acid and inking up is effected with greasy ink. A positive printing plate is obtained.

Example 21

An aluminum support which had been roughened by brushing is coated with a solution containing 1 part by weight of diphenylamine-4-diazonium chloride and 0.5 part by weight of the diphosphonic acid corresponding to formula

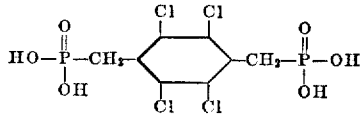


in 3 parts by volume of water and 3 parts by volume of dimethylformamide. The coating is dried with a warm air current.

For the preparation of a printing plate from the presensitized material thus obtained, the material is developed, after exposure, with a 1.5 percent phosphoric acid solution.

Example 22

The procedure described in the preceding example is repeated using, however, instead of the diphosphonic acid mentioned in Example 21, an equal quantity of the diphosphonic acid corresponding to the following formula:



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. A presensitized printing plate which comprises a metallic base material having a coating thereon, the coating comprising a light-sensitive diazo compound and at least one organic acid selected from the group consisting of a phosphonic acid other than polyvinylphosphonic acid, a phosphinic acid and an arsonic acid.

2. A presensitized printing plate according to claim 1 in which the base material is aluminum.

3. A presensitized printing plate according to claim 2 in which the acid is a phosphonic acid of low molecular weight.

4. A presensitized printing plate according to claim 2 in which the acid is chloromethanephosphonic acid.

5. A presensitized printing plate according to claim 2 in which the acid is benzenephosphonic acid.

6. A presensitized printing plate according to claim 2 in which the acid is 4-hydroxy-phenylarsonic acid.

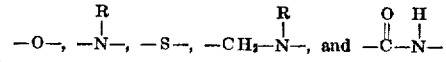
7. A presensitized printing plate according to claim 2 in which the acid is 4-methylphenoxymethylphosphonic acid.

8. A presensitized printing plate according to claim 2 in which the acid is naphthalene-2-phosphonic acid.

9. A presensitized printing plate according to claim 2 in which the acid is benzylarsonic acid.

10. A presensitized printing plate according to claim 2 in which the diazo compound contains at least two phenyl groups linked to each other.

11. A presensitized printing plate according to claim 2 in which the diazo compound contains at least two phenyl groups linked to each other through an intermediate group selected from the group consisting of



in which R is selected from the group consisting of hydrogen, alkyl, acyl, aralkyl or acyl groups.

12. A process for making a printing plate which comprises exposing a coated metallic base material to light under a master and developing the resulting image with a developer liquid, the coating comprising a light-sensitive diazo compound and at least one organic acid selected from the group consisting of a phosphonic acid other than polyvinylphosphonic acid, a phosphinic acid, and an arsonic acid.

13. A process according to claim 12 in which the base material is aluminum.

14. A process according to claim 12 in which the acid is a phosphonic acid of low molecular weight.

15. A process according to claim 12 in which the acid is chloromethanephosphonic acid.

16. A process according to claim 12 in which the acid is benzenephosphonic acid.

17. A process according to claim 12 in which the acid is 4-hydroxy-phenylarsonic acid.

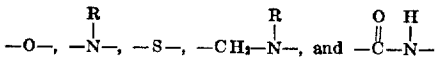
18. A process according to claim 12 in which the acid is 4-methyl-phenoxymethylphosphonic acid.

19. A process according to claim 12 in which the acid is naphthalene-2-phosphonic acid.

20. A process according to claim 12 in which the acid is benzylarsonic acid.

21. A process according to claim 12 in which the diazo compound contains at least two phenyl groups linked to each other.

22. A process according to claim 12 in which the diazo compound contains at least two phenyl groups linked to each other through an intermediate group selected from the group consisting of



in which R is selected from the group consisting of hydrogen, alkyl, acyl, aralkyl and acyl groups.

References Cited

UNITED STATES PATENTS

3,179,518	4/1965	Sus et al.	96—33
3,220,832	11/1965	Uhlig	96—33 X

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,404,003 October 1, 1968

Hartmut Steppan

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, lines 35 and 36, "produce" should read -- product --. Column 10, line 23, "acyl", first occurrence, should read -- aryl --; line 59, "acyl", first occurrence, should read -- aryl --.

Signed and sealed this 10th day of February 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents