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DIAZO PRINTING PLATES AND METHOD FOR THE PRODUCTION THEREOF

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This invention relates to a novel presensitized printing plate containing a diazo compound, and to a method for the production thereof, and, more particularly, to a novel presensitized printing plate which can be developed merely by washing with water, thereby eliminating the alkali or acid treatment required with printing plates known to the prior art.

It is known that the solubility of water-soluble colloids changes when the colloids are exposed to light in the presence of diazo compounds. However, the results of this hardening or "tanning" action are generally unsatisfactory insofar as the practical use of such hardened colloids in the reproduction art is concerned. It has, therefore, been proposed to subject the colloid layers containing diazo compounds to an after-treatment with a chromate solution after exposure to light under a transparent original or master. Diazo compounds of higher molecular weight, such as condensation products of aldehydes with diazo compounds, for example the diazo compounds of p-amino-diphenylamine, have been proposed for the tanning of colloid layers, and best results are obtained when these diazo compounds constitute about 10 percent by weight of the dry colloid applied to the base material, such as aluminum, for example.

However, the foregoing plates consisting of base materials coated with layers consisting of water-soluble colloids sensitized by means of diazo compounds have not found practical application in the printing trade. The light-hardened colloid particles of these layers are not capable of holding the greasy ink in flat and offset printing, and the mechanical strength of the hardened colloids is insufficient to permit long runs.

In accordance with the present invention, it has been found that excellent flat and offset printing plates can be produced from light-sensitive material consisting of a support having a colloid layer thereon, the colloid layer comprising a polyacrylic acid and containing a diazonium chloride or bromide of a p-amino-diphenylamine as the light-sensitive substance. The percentage of the diazo compounds to be employed according to the present invention is from about 75 to 400 percent by weight, preferably between about 100 to 200 percent by weight of the dry weight of the polyacrylic acid. Both components may be applied in either an aqueous solution or dissolved in a suitable organic solvent, such as ethylene glycol monomethyl ether, or they also may be applied in mixtures of organic solvents with water. The percentage of a polyacrylic acid in the coating solution may vary widely, and preferably it is about 1 to 2 percent by weight. If granulated zinc plates are used, best results are obtained by using a concentration of about 2 to 3 percent by weight.

The solutions of polyacrylic acid and the diphenylamine-p-diazonium chloride or bromide are coated on the base material according to known procedures, and the base material may be metal, such as aluminum or zinc, or may be a specially treated paper foil, the treatment of the latter being a conventional treatment for such foil. The coated support is then dried, preferably at an elevated temperature, such as about 90° C., for example.

The diazo chlorides or bromides of p-diazo-diphenylamine which may be used in the present invention, may be either substituted or unsubstituted, and the substituents in the aryl nuclei of the diphenylamine radical may be, for example, alkyl, alkoxy, halogen, hydroxy or sulfarylido radicals. Also, a diazonium salt radical, in addition to the diazonium chloride or bromide radical, may be a substituent. The molecule may contain one or more of these substituents, and compounds containing different substituents may also be employed. Among the substituted diazonium chlorides of p-diazo-diphenylamines which may be used, are the following:

4'-bromo-diphenylamine-4-diazonium chloride
4'-chloro-diphenylamine-4-diazonium chloride
4'-methoxy-diphenylamine-4-diazonium chloride
3-methoxy-diphenylamine-4-diazonium chloride
3-n-propoxy-diphenylamine-4-diazonium chloride
x,x_1,x_2-tribromo-diphenylamine-4-diazonium chloride
4'-methyl-diphenylamine-4-diazonium chloride
4'-hydroxy-diphenylamine-4-diazonium chloride
4'-benzoylamino-diphenylamine-4-diazonium chloride
4'-fluoro-diphenylamine-4-diazonium chloride
2-anilido-sulfonyl-diphenylamine-4-diazonium chloride
2-(p-toluene-sulfonyl-amino)-diphenylamine-4-diazonium chloride
4'-benzoylamino-2,5-diethoxy-diphenylamine-4-diazonium chloride
4'-chloro-2'-methoxy-diphenylamine-4-diazonium chloride.

The colloid in the light-sensitive layer of the printing plates of this invention may be polyacrylic acid or polymethacrylic acid per se, or an acrylic-methacrylic acid copolymerizate, or the like.

The unexposed coated foils prepared in accordance with this invention, have an excellent shelf life, and after exposing the light-sensitive foil in the usual manner under a negative original or master, development can be effected by simply rinsing, swabbing or bathing the exposed foil with water. This can be accomplished, for example, by mounting the exposed foil on a printing machine and wiping it over with a sponge soaked in water. After this development, the first plates may be run off immediately, and no additional treatment with one of the so-called fixing agents, which is often required in offset printing, is necessary. Even without such after-treatment, prints are obtained which are free of scum and the printing plates produced in accordance with this invention give very long runs.

Certain of the substituted and unsubstituted diphenylamine-4-diazonium chlorides and bromides which may be used in accordance with the present invention, are known to the prior art. All these diazonium halogenides are prepared from the corresponding 4-amino-diphenylamines following well known chemical procedures; for example, by reduction of the corresponding 4-nitro-diphenylamines and subsequent diazotization of the 4-aminodiphenylamines obtained. The 4-nitro-diphenylamines are prepared by reacting chloro-4-nitro-benzene-sulfonic acids-(3) with aromatic amines, and then splitting off the sulfo group of the 4-nitro-diphenylamine sulfonic acids thus formed, by heating the sulfonic acids with sulfuric acid.

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

EXAMPLE I

Preparation of 2-Anilido-Sulfonyl-Diphenylamine-4-Diazonium Chloride

In the preparation of this compound, 4-nitro-diphenylamine-2-sulfanilide is first prepared. A benzene solution containing 4-nitro-diphenylamine-2-sulfochloride and aniline is permitted to stand until reaction is effected, i.e.,

several hours. The 4-nitro-diphenylamine-2-sulfanilide thus formed is dissolved in dioxane, and then catalytically reduced to the corresponding 4-amino-diphenylamine-2-sulfanilide. This compound, in the form of its hydrochloride, is then dissolved in dimethylformamide and slowly diazotized with a sodium nitrite solution in the presence of hydrochloric acid. The compound 2-anilido-sulfonyl-diphenylamine-4-diazonium chloride precipitates, which, after purification with ether, melts at a temperature of 178 to 180° C.

EXAMPLE II

Preparation of 2-(p-Toluene-Sulfonyl-Amino)-Diphenylamine-4-Diazonium Chloride

The starting material for this compound is 2-amino-4-nitro-diphenylamine, and this compound is dissolved in dioxane and then reacted at a temperature of 50 to 60° C. with p-toluene-sulfochloride in the presence of pyridine. The nitro compound formed is reduced with sodium hyposulfite in dioxane and the corresponding amine is precipitated from the solution by the addition of glacial acetic acid. The amino compound is then diazotized with isoamyl-nitrite in an alcoholic solution containing hydrochloric acid. The compound-2-(p-toluene-sulfonyl-amino)-diphenylamine-4-diazonium chloride which forms decomposes at a temperature of 160 to 162° C. after purification with ether.

EXAMPLE III

Using a plate whirler, an aluminum foil, which was previously mechanically roughened by brushing, was coated with an ethylene glycol monomethyl ether solution containing 1 percent by weight of polyacrylic acid of medium viscosity (intrinsic viscosity=0.5) and 1 percent by weight of the chloride of the diazo compound of p-amino-diphenylamine. The foil was then dried in a current of warm air and the dried layer was then exposed for a period of one minute under a negative original, using an arc lamp of 18 amperes at a distance of about 70 cm. The exposed layer was then developed by wiping it over with a cotton pad soaked in water. Development may be similarly effected by rinsing with water. After development, the wet plate was immediately mounted an an offset printing machine, inked, and the first copies were run off without previously fixing the image with gum arabic or aqueous phosphoric acid, as is commonly done. Very high runs were obtained.

Similarly, good results were obtained when instead of the coating solutions described above, solutions were used containing:

(*a*) 0.5 percent of polyacrylic acid and 1.5 percent by weight of the diazo compound, and

(*b*) 1.5 percent by weight of the polyacrylic acid and 2 percent by weight of the diazo compound.

Instead of the polyacrylic acid of the viscosity described, there may be polyacrylic acids of higher or lower viscosities.

In order to have clean aluminum foils before applying the coating, the foils may be pretreated with dilute solutions of caustic alkalies and nitric acids, or with solutions of tertiary alkali metal phosphates.

EXAMPLE IV

Following the general procedure of Example III above, a grained zinc plate was coated with a solution containing 3 parts by weight of highly viscous polyacrylic acid (intrinsic viscosity=1.1) and 3 parts by weight of the diazonium chloride of p-amino-diphenylamine, dissolved in 100 parts by weight of ethylene glycol monomethyl ether. The coated plate was then dried, and after exposing the dried layer under a negative original, it was developed by rinsing with water. The plate was then ready for use on a printing machine.

EXAMPLE V

Following the general procedure of Example III above, a paper printing foil was coated with the solution described in Example III, dried and then developed in accordance with the procedure of Example III. In this case also, printing could be begun immediately without the application of a special fixing agent, and long runs were obtained.

EXAMPLE VI

An aluminum foil which had been mechanically roughened by brushing was coated by means of a plate whirler with an ethylene glycol monomethyl ether solution containing 0.6 percent by weight of polyacrylic acid of medium viscosity (intrinsic viscosity=0.5) and 0.6 percent by weight of diphenylamine-4-diazonium bromide. The coating was then dried in a current of warm air and the dried layer was exposed to light under a negative original, after which the exposed layer was developed by wiping it over with a cotton pad soaked in water. The developing treatment removes the unexposed parts of the layer and after development, and without the application of a fixing agent such as gum arabic or phosphoric acid, the foil was clamped into an offset printing machine and used to make copies.

Equally good results were obtained when the aforementioned coating solution was substituted by ethylene glycol monomethyl ether solution containing 1 percent by weight of the diazo compound described. The polyacrylic acid may also be replaced by the same quantity of polymethacrylic acid or a 1:1 copolymerizate of acrylic acid and methacrylic acid.

Printing plates of similar quality are obtained if ethylene glycol monomethyl ether solutions are used for coating, having corresponding compositions to those described above, but in which the diphenylamine-4-diazonium bromide is replaced by equivalent quantities of one of the following diazonium chlorides:

4'-bromo-diphenylamine-4-diazonium chloride
4'-chloro-diphenylamine-4-diazonium chloride
4'-methoxy-diphenylamine-4-diazonium chloride
3-methoxy-diphenylamine-4-diazonium chloride
3-n-propoxy-diphenylamine-4-diazonium chloride
x,x_1,x_2-tribromo-diphenylamine-4-diazonium chloride
4'-methyl-diphenylamine-4-diazonium chloride
4'-hydroxy-diphenylamine-4-diazonium chloride
4'-benzoylamino-diphenylamine-4-diazonium chloride
4'-fluoro-diphenylamine-4-diazonium chloride
2-anilido-sulfonyl-diphenylamine-4-diazonium chloride
2 - (p - toluene - sulfonyl - amino) - diphenylamine - 4-diazonium chloride
4' - benzoylamino - 2,5 - diethoxy - diphenylamine - 4-diazonium chloride
4 - chloro - 2' - methoxy - diphenylamine - 4 - diazonium chloride.

In each case, the support for the light-sensitive layer may be an aluminum foil, previously treated at a temperature of about 20° C., first for 5 minutes with a 5 percent by weight caustic soda solution, and then for another 5 minutes with a 5 percent nitric acid solution, and then finally rinsed with water and dried.

EXAMPLE VII

The general procedure of Example VI was followed, except that a coating solution was used containing:

(*a*) 0.2 part by weight of diphenylamine-4-diazonium chloride,

(*b*) 0.1 part by weight of 4'-bromo-diphenylamine-4-diazonium chloride,

(*c*) 0.15 part by weight of 4'-fluoro-diphenylamine-4-diazonium chloride, and

(*d*) 0.5 part by weight of highly-viscous polyacrylic acid (intrinsic viscosity=1.1), dissolved in 100 parts by volume of ethylene glycol monomethyl ether.

A printing plate was prepared having a quality equivalent to that described in Example VI.

EXAMPLE VIII

An anodically oxidized aluminum foil was coated by means of a plate whirler with an aqueous solution containing 0.3 percent by weight of polyacrylic acid of medium viscosity (intrinsic viscosity=0.5), and 0.6 percent by weight of 4'-bromo-diphenylamine-4-diazonium chloride, and the plate was then dried at a temperature of 100° C. in a drying oven. The dried light-sensitive layer was then exposed to light under a negative original, and the exposed layer was developed by means of a water-shower. The developed foil was then clamped directly to an offset printing machine and used for printing.

EXAMPLE IX

A paper base for printing plates, such as that sold by the S. D. Warren Company of Cumberland Mills, Maine, was coated by means of a plate whirler with a solution containing 1 g. of polyacrylic acid of medium viscosity (instrinsic viscosity=0.5), and 1 g. of 4'-bromo--diphenylamine-4-diazonium chloride per 100 cc. of ethylene glycol monomethyl ether solvent, and the foil was then dried. After drying, the foil was exposed to light under a negative original, developed with water, inked with greasy ink, and used for the production of copies.

Instead of the ethylene glycol monomethyl ether solution used above, there may also be used an aqueous solution of polyacrylic acid and 4'-bromo-diphenylamine-4-diazonium chloride.

EXAMPLE X

0.5 part by weight of p-diphenylamine-diazonium chloride and 0.5 part by weight of polymethacrylic acid (intrinsic viscosity=0.7) were dissolved in 100 parts by volume of ethylene glycol monomethyl ether. A mechanically roughened aluminum foil was coated with this solution, using a plate whirler, and the coated foil was then dried and exposed under a transparent negative original. The exposed foil was then developed under a water shower, and used for the production of copies.

The polymethacrylic acid used above may be replaced by the same quantity of 1:1 copolymerizate of acrylic acid and methacrylic acid (intrinsic viscosity=1.77), and printing plates of high quality are obtained.

A paper printing foil may also be substituted for the aluminum foil and high quality plates are obtained.

EXAMPLE XI

The method described in Example VIII was repeated, but for coating the aluminum foil a solution was used containing, in 100 cc. of ethylene glycol monomethyl ether, 0.3 gram of 4'-bromo-diphenylamine-4-diazonium bromide and 0.5 gram of polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). Instead of the diazonium compound just mentioned, there may be used the same quantity of 4'-chloro-diphenylamine-4-diazonium bromide.

4'-bromo-diphenylamine-4-diazonium bromide is prepared as follows:

10 grams of 4'-bromo-diphenylamine-4-diazonium chloride are dissolved, while heating, in 150 cc of glacial acetic acid saturated with gaseous hydrobromic acid. The solution is treated with animal charcoal, filtered, and then mixed with 300 cc. of acetic acid ethyl ester, whereupon the diazonium bromide precipitates. After recrystallization from 200 cc. of ethanol, this diazonium bromide decomposes at 138–139° C.

4'-chloro-diphenylamine-4-diazonium bromide is prepared as follows:

10 grams of 4'-chloro-diphenylamine-4-diazonium chloride are dissolved in 100 cc. of 48 percent aqueous hydrobromic acid, while heating, and the solution is then treated with animal charcoal. Upon cooling the filtrate, the diazonium bromide crystallizes out. For purification, it is dissolved in glacial acetic acid and reprecipitated by adding ethyl ether to the solution. The purified diazonium bromide decomposes at 128–129° C.

EXAMPLE XII

The method described in Example VIII was repeated, but for coating the aluminum foil a solution was used, containing, in 100 cc. of ethylene glycol monomethyl ether, 1 gram of 2'-methoxy-diphenylamine-4-diazonium bromide and 0.6 gram of polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). Instead of the 2'-methoxy-diphenylamine-4-diazonium bromide, the coating solution may contain the same quantity of 4'-methoxy-diphenylamine-4-diazonium bromide.

2'-methoxy-diphenylamine-4-diazonium bromide is prepared as follows:

20 grams of 2'-methoxy-diphenylamine-4-diazonium chloride are dissolved in 20 cc. of 48 percent aqueous hydrobromic acid, while heating. The solution is treated with animal charcoal and filtered. Upon cooling the filtered solution the diazonium bromide separates. It is purified by dissolving it in glacial acetic acid and adding ethyl ether to the solution. It melts at 117° C. with decomposition.

4'-methoxy-diphenylamine-4-diazonium bromide is prepared as follows:

20 grams of 4'-methoxy-diphenylamine-4-diazonium chloride are dissolved in 200 cc. of 48 percent aqueous hydrobromic acid while heating. The solution is treated with animal charcoal, filtered, and the filtrate is evaporated under reduced pressure and at a temperature of 60 C. The dry solid is dissolved in 200 cc. of hot methanol and the solution is then mixed with 500 cc. of ethyl ether. The reprecipitated diazonium bromide decomposes at 152° C.

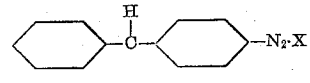
It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

The expression "a polyacrylic acid" as used in the following claims is intended to include likewise a polymethacrylic acid as well as copolymerizates of acrylic and methacrylic acid.

What is claimed is:

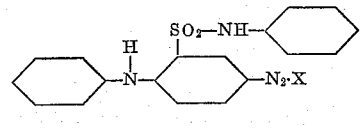
1. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound selected from the group consisting of the diazonium chloride and bromide of a p-amino-diphenylamine.

2. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo radicals.

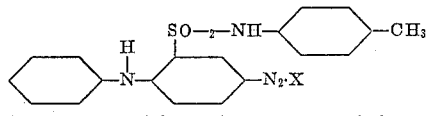
3. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo radicals.

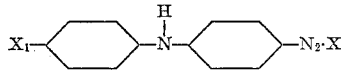
4. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a

layer comprising a polyacrylic acid and a compound having the formula



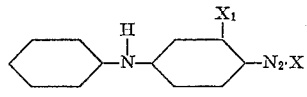
in which X is selected from the group consisting of chloro and bromo radicals.

5. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



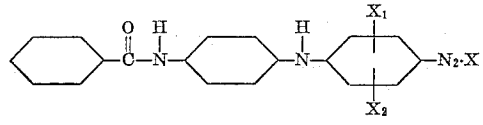
in which X is selected from the group consisting of chloro and bromo radicals and X_1 is selected from the group consisting of fluoro, chloro, bromo, alkyl, hydroxy and alkoxy radicals.

6. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



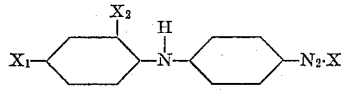
in which X is selected from the group consisting of chloro and bromo radicals and X_1 is an alkoxy radical.

7. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



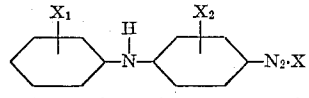
in which X is selected from the group consisting of chloro and bromo radicals, and X_1 and X_2 are selected from the group consisting of hydrogen and alkoxy radicals.

8. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo radicals, X_1 is halogen, and X_2 is an alkoxy radical.

9. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula

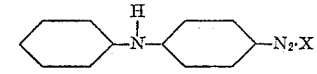


in which X is selected from the group consisting of chloro and bromo radicals, X_1 is selected from the group consisting of hydrogen, fluoro, chloro, bromo, hydroxy, alkyl, and alkoxy radicals, and X_2 is selected from the group consisting of hydrogen, sulfonamide, and alkoxy radicals.

10. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound selected from the group consisting of the diazonium chloride and bromide of a p-amino-diphenylamine, and washing the exposed plate with water.

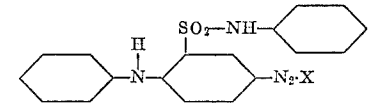
11. A process for developing a printing plate which

comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



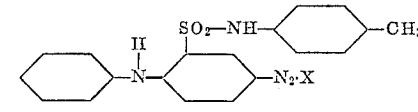
in which X is selected from the group consisting of chloro and bromo radicals, and washing the exposed plate with water.

12. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



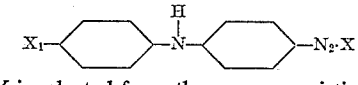
in which X is selected from the group consisting of chloro and bromo radicals, and washing the exposed plate with water.

13. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



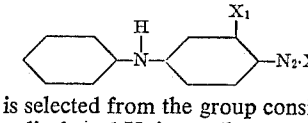
in which X is selected from the group consisting of chloro and bromo radicals, and washing the exposed plate with water.

14. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



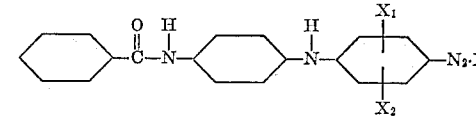
in which X is selected from the group consisting of chloro and bromo radicals and X_1 is selected from the group consisting of fluoro, chloro, bromo, alkyl, hydroxy and alkoxy radicals, and washing the exposed plate with water.

15. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



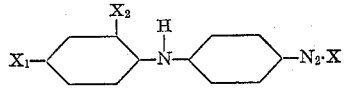
in which X is selected from the group consisting of chloro and bromo radicals and X_1 is an alkoxy radical, and washing the exposed plate with water.

16. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



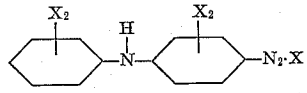
in which X is selected from the group consisting of chloro and bromo radicals, and X_1 and X_2 are selected from the group consisting of hydrogen and alkoxy radicals, and washing the exposed plate with water.

17. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo radicals, X_1 is halogen, and X_2 is an alkoxy radical, and washing the exposed plate with water.

18. A process for developing a printing plate which comprises exposing to light under a master a pre-sensitized printing plate comprising a hydrophilic base material directly coated with a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo radicals, X_1 is selected from the group consisting of hydrogen, fluoro, chloro, bromo, hydroxy, alkyl, and alkoxy radicals, and X_2 is selected from the group consisting of hydrogen, sulfonamide, and alkoxy radicals, and washing the exposed plate with water.

19. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and diphenylamine-4-diazonium chloride.

20. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and diphenylamine-4-diazonium bromide.

21. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-bromo-diphenylamine-4-diazonium chloride.

22. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-chloro-diphenylamine-4-diazonium chloride.

23. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2-anilido-sulfonyl-diphenylamine-4-diazonium chloride.

24. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2-(p-toluene-sulfonyl-amino)-diphenylamine-4-diazonium chloride.

25. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-bromo-diphenylamine-4-diazonium bromide.

26. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-chloro-diphenylamine-4-diazonium bromide.

27. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2'-methoxy-diphenylamine-4-diazonium bromide.

28. A presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-methoxy-diphenylamine-4-diazonium bromide.

29. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directed coated thereon a layer comprising a polyacrylic acid and diphenylamine-4-diazonium chloride, and washing the exposed plate with water.

30. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and diphenylamine-4-diazonium bromide, and washing the exposed plate with water.

31. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-bromo-diphenylamine-4-diazonium chloride, and washing the exposed plate with water.

32. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directed coated thereon a layer comprising a polyacrylic acid and 4'-chloro-diphenyl-amine-4-diazonium chloride, and washing the exposed plate with water.

33. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2-anilido-sulfonyl-diphenylamine-4-diazonium chloride, and washing the exposed plate with water.

34. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2-(p-toluene-sulfonyl-amino)-diphenylamine-4-diazonium chloride, and washing the exposed plate with water.

35. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-bromo-diphenylamine-4-diazonium bromide, and washing the exposed plate with water.

36. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-chloro-diphenylamine-4-diazonium bromide, and washing the exposed plate with water.

37. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 2'-methoxy-diphenylamine-4-diazonium bromide, and washing the exposed plate with water.

38. A process for developing a printing plate which comprises exposing to light under a master presensitized printing plate comprising a hydrophilic base material having directly coated thereon a layer comprising a polyacrylic acid and 4'-methoxy-diphenylamine-4-diazonium bromide, and washing the exposed plate with water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,063,631	Schmidt et al.	Dec. 8, 1936
2,649,373	Neugebauer et al.	Aug. 18, 1953
2,667,415	Neugebauer et al.	Jan. 26, 1954
2,687,958	Neugebauer	Aug. 31, 1954
2,720,467	Frank et al.	Oct. 11, 1955
2,760,431	Beatty	Aug. 28, 1956
2,772,974	Kosalek et al.	Dec. 4, 1956
2,937,085	Seven et al.	May 17, 1960