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DIAZO PRINTING PLATES AND METHOD FOR THE PRODUCTION THEREOF

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14 Claims. (Cl. 96—33)

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 compound 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.

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 as light sensitive substances the diazonium chlorides or diazonium bromides of 3-amino-carbazoles, i.e. 3-amino-carbazole and the substitution products thereof containing alkyl groups or alkoxy groups. Instead of polyacrylic acid, there may be used polymethacrylic acid or copolymers of acrylic-methacrylic acid.

Some of the diazonium salts to be used according to the present invention have been described in the literature. Insofar as they constitute new products, they can be prepared by the known methods of diazotization from the respective amino-carbazoles.

In practicing the present invention, sheet metal in the form of a plate or a foil, preferably sheet aluminum, or a paper sheet, preferably the specific papers commercially available for the manufacture of paper printing plates are used as base supports. For the purpose of providing the base with the light sensitive layer, the respective carbazole-3-diazonium chloride or carbazole-3-diazonium bromide, or mixtures of such diazonium salts, is dissolved in an organic solvent and the solution is applied to the base by a whirling, spraying or brushing operation. The coated layer supports are then dried, in general at elevated temperatures, e.g. at about 90° C. Suitable organic solvents are primarily solvents having a boiling point between 80 and 150° C. Preferred are

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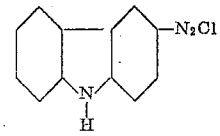
the ethylene glycol monoalkyl ethers, dioxane, and diacetone alcohol; the organic solvents may be mixed with water and the mixture used for dissolving the 3-diazonium-carbazole salt. The diazonium chlorides and the diazonium bromides obtained from the 3-amino-carbazoles employed form, with polyacrylic acid and polymethacrylic acid respectively, addition products which are difficultly soluble in water. For this reason it is essential that the quantity of water added to the organic solvent be insufficient to cause separation of the addition products. Advantageously, solutions of the diazonium salts are used which contain about 0.5 to 2 percent, by weight, of the respective diazonium chloride or bromide, or mixtures thereof. Although the weight ratio between the quantity of the colloid and the diazonium salt present in the solution may be varied within wide limits, it is preferred to use both components in approximately equal quantities, i.e. 1:1.

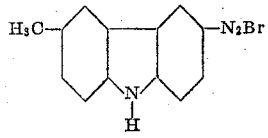
The light sensitive colloidal layers produced according to this invention are of excellent stability and storageability. For making printing plates from the reproduction material, the colloidal layers are exposed to light under a light-image and after exposure an image is produced on the support by merely developing it with water, e.g. by showering or wiping the plate over with water or by immersing it in a water bath. Alternatively, the exposed plate may be developed by clamping it into the printing apparatus and wiping it over with a sponge soaked in water. It is superfluous to subject the base after development to an after-treatment with dilute acid for the purpose of improving the water conductivity of the surface of the base where the colloidal layer has been removed. Thus, a substantial simplification of the developing operation is achieved. After the treatment with water (development), the coated surface of the base is inked with greasy ink and the printing plates are ready for printing long runs of copies; faultless prints are obtained.

The following light sensitive compounds are exemplary of those which may be employed in the present invention:

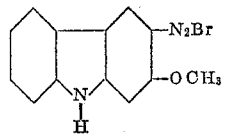
Formula 1



Formula 2



Formula 3



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

Example I

0.6 part by weight of the compound corresponding to Formula 1 above and 0.6 part by weight of a water-soluble polymethacrylic acid (intrinsic viscosity=0.7) were dissolved in 100 parts by volume of ethylene glycol monomethyl ether. This solution was coated on an alu-

minum foil, the surface of which had been mechanically roughened. The coated foil was then dried and the drying operation was finished by exposing the coated surface of the foil to a current of hot air at a temperature of 100° C. for about two minutes. The sensitized foil was exposed to a negative light-image using an arc lamp of 18 amperes for two minutes, for example, at a distance of 70 cm. The exposed surface of the foil was then rinsed with water and rinsing was continued until the yellow-colored areas of the exposed coating, i.e. the areas unaffected by light during the exposure, were removed completely, by the water; a positive image of the negative pattern remained on the foil and was clearly visible on the metal base. The imaged foil was then inked with greasy ink and the printing plate thus obtained was suitable for use in all conventional offset printing machines.

The compound corresponding with Formula 1 is prepared by diazotization of 3-amino-carbazole in hydrochloric acid solution; 3-amino-carbazole has been described by Morgan and Reod in the Journal of the Chemical Society, London, volume 121, page 2712. The diazonium chloride is purified by dissolving it in water and adding a saturated sodium chloride solution. The carbazole-3-diazonium chloride is an orange-yellow powder, melting at 102–104° C. with decomposition.

An equally good printing plate, giving runs of the same order, was obtained by coating the aluminum foil with a solution containing, per 100 cc. of ethylene glycol monomethyl ether, 1.2 parts by weight of carbazole-3-diazonium chloride and 0.6 part by weight of polymethacrylic acid (intrinsic viscosity=0.7).

Example II

An aluminum foil, the surface of which had been mechanically roughened, was coated with a solution, containing per 100 cc. of ethylene glycol monomethyl ether, 0.6 part by weight of the compound corresponding to Formula 2 above and 0.6 part by weight of a water soluble polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). The coated foil was dried and subsequently exposed to a light-image in the manner described in Example I above. Development of the exposed foil was effected by means of tap water, see also Example I. From a negative pattern a positive printing plate was obtained.

The compound corresponding with Formula 3 may be substituted for the compound of Formula 2 in the coating solution stated above. The sensitized foil thus obtained is very stable and storageable over a long period of time.

The compound corresponding with Formula 2 above is made by diazotizing 3-amino-6-methyl-carbazole in an aqueous hydrobromic acid solution; 3-amino-6-methyl-carbazole has been described by Bremer in "Justice Liebig's Annalen der Chemie," volume 514 (1934), page 279. The diazonium bromide obtained is purified by dissolving it in water and by adding a saturated potassium bromide solution. The compound is an orange-yellow powder which upon heating in a melting point tube, starts darkening at 115° C. and decomposes at 170° C.

The compound corresponding with Formula 3 above is manufactured from 3-amino-2-methoxy-carbazole. Because the statements relating to the preparation of the starting material, contained in German Patent No. 553,628, and also in "Chemisches Zentralblatt," volume 32, II, page 1516, are somewhat ambiguous, 3-amino-2-methoxy-carbazole is prepared as follows:

2-methoxy-N-acetyl-carbazole (melting point 81–84° C.) is obtained by heating a mixture of 2-methoxy-carbazole (melting point 233–234° C.) and acetic acid anhydride at about 200° C. The acetylated product is treated with nitric acid at room temperature for several hours which treatment results in the formation of 2-methoxy-3-nitro-N-acetyl-carbazole (melting point 154–155° C.). This nitro compound is catalytically reduced with hydrogen and Raney nickel catalyst to 2-methoxy-3-amino-N-acetyl-carbazole (melting point 180–181° C.). The amino-carbazole obtained is heated with a 10 percent methanolic potassium hydroxide solution for several hours, thereby splitting off the acetyl group. The resulting 2-methoxy-3-amino-carbazole is separated in the form of its hydrochloride, which decomposes above 225° C. By diazotization of the 2-methoxy-3-amino-carbazole hydrochloride in hydrobromic acid solution, 2-methoxy-carbazole-3-diazonium bromide is obtained which is purified by dissolving it in water and by adding a saturated potassium bromide solution. The diazonium bromide is a greenish-yellow powder which begins darkening and decomposing upon heating to about 100° C.

Example III

An anodically oxidized aluminum foil was coated with a solution containing, per 100 parts by volume of ethylene glycol monomethyl ether, 0.6 part by weight of the compound corresponding to Formula 1 above and 0.8 part by weight of a water soluble polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). Coating of the aluminum foil was effected by means of a conventional plate whirler. The foil after being coated with the solution was dried, exposed to a negative light-image and, after exposure, rinsed with water for about one minute. A positive image was obtained which was inked up with greasy ink. The foil could then be used as a printing plate.

Example IV

The processed surface of a commercial paper printing foil was coated with a solution containing, per 100 parts by volume of diacetone alcohol, 0.5 part by weight of the compound corresponding to Formula 2 above and 0.7 part by weight of a water soluble polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). The coated foil was dried and subsequently exposed to a light-image; after exposure, the exposed surface of the foil was inked up with greasy ink and subsequently rinsed with water. By this treatment with water, those areas of the acrylic acid layer which were not struck by light in the course of the exposure, were dissolved and the greasy ink sticking to the areas unaffected by light was also removed. A positive printing plate is obtained if the light-image used as a pattern is a negative.

Example V

A zinc plate was treated with a 4 percent acetic acid solution containing 4 percent by weight of potassium aluminum sulfate, then brushed for about 3 to 5 minutes, rinsed with water and dried. Then the plate was coated with a solution containing, per 100 parts by volume of diacetone alcohol, 2 parts by weight of the compound corresponding to Formula 2 above and 0.5 part by weight of a water soluble polyacrylic acid of medium viscosity (intrinsic viscosity=0.5). After coating, the sensitized plate was dried and exposed to a negative light-image. The exposed plate was rinsed with water and afterwards inked up with greasy ink. Long runs of copies can be made from the positive printing plate thus obtained.

Example VI

0.5 part by weight of the compound corresponding to Formula 1 above and 0.5 part by weight of a water soluble copolymer of acrylic acid and methacrylic acid (molar ratio 1:1) were dissolved in 100 parts by volume of ethylene glycol monomethyl ether. An aluminum foil, both sides of which had been mechanically roughened, was coated with this solution. After the solution had dried, the coated side of the aluminum foil was exposed under a negative transparent original and subsequently rinsed with tap water for about 30–60 seconds. Without further treatment, the imaged side of the foil was inked with greasy ink and used as a printing plate. A positive printing plate was obtained from a negative original.

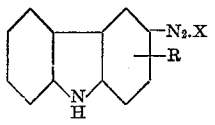
The expression "a polyacrylic acid" as used in the following claims is intended to include a polymethacrylic acid as well as copolymerizates of acrylic and methacrylic acid.

It will be obvious to those skilled in the art that many modifications can 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:

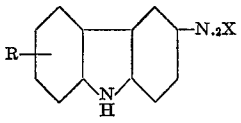
1. A presensitized printing plate comprising a base material having directly coated thereon a layer comprising a polyacrylic acid and a compound selected from the group consisting of the diazonium chloride and bromide of a 3-amino-carbazole.

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



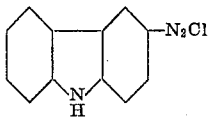
in which X is selected from the group consisting of chloro and bromo ions and R is an alkoxy radical.

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

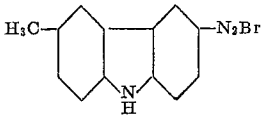


in which X is selected from the group consisting of chloro and bromo ions and R is an alkyl radical.

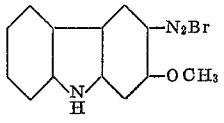
4. A presensitized printing plate comprising a base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



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



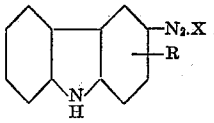
6. A presensitized printing plate comprising a base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



7. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a 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 3-amino-carbazole, and washing the exposed plate with water.

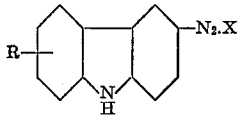
8. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a base material having directly

coated thereon a layer comprising a polyacrylic acid and a compound having the formula



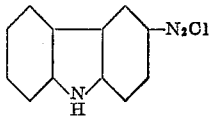
in which X is selected from the group consisting of chloro and bromo ions and R is an alkoxy radical, and washing the exposed plate with water.

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



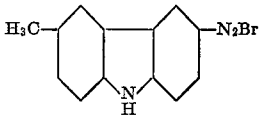
in which X is selected from the group consisting of chloro and bromo ions and R is an alkyl radical, and washing the exposed plate with water.

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



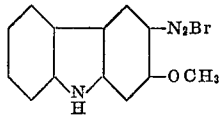
and washing the exposed plate with water.

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



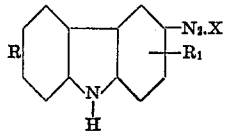
and washing the exposed plate with water.

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



and washing the exposed plate with water.

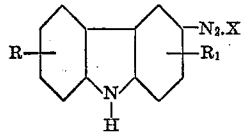
13. A presensitized printing plate comprising a base material having directly coated thereon a layer comprising a polyacrylic acid and a compound having the formula



in which X is selected from the group consisting of chloro and bromo and R and R_1 are selected from the group consisting of hydrogen, alkyl, and alkoxy radicals, at least one of R and R_1 being hydrogen.

14. A process for developing a printing plate which comprises exposing to light under a master a presensitized printing plate comprising a 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 and R and R_1 are selected from the group consisting of hydrogen, alkyl, and alkoxy radicals, at least one of R and R_1 being hydrogen, and washing the exposed plate with water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,531,485	Von Glahn et al.	Nov. 28, 1950
2,593,928	Slifkin	Apr. 22, 1952
2,772,974	Kosalek et al.	Dec. 4, 1956
2,822,272	Kosalek et al.	Feb. 4, 1958
2,937,085	Seven et al.	May 17, 1960

OTHER REFERENCES

Saunders: The Aromatic Diazo Compounds, Edward Arnold & Co., London, 1949, pages 78–79.