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PAPER PRINTING FOILS FOR LITHOGRAPHIC PURPOSES AND A PROCESS OF PREPARING THEM

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This invention relates to the production of photolithographic printing plates comprising paper photosensitized by diazo compounds, to methods of improving the aging or storing qualities of such paper, and to the photosensitized paper product itself.

It is known to make use of the light decomposition products of certain diazo compounds for producing so called tanned pictures. In this known process a paper base is coated with a solution of a soluble colloid such as gelatine or gum arabic, containing the diazo component. After drying the layers thus obtained are exposed to light, whereby the light decomposition product of a suitable diazo compound hardens or tans the soluble colloid. At the places not hit by the exposure the colloid remains soluble and can be removed afterwards with water or other solvents. This process yields positive "tanned" pictures from negative originals.

One object of the present invention is the use of diazo compounds for the production of printing foils or plates on a paper base without the use of a colloid capable of being hardened under exposure. These foils shall be used in flat and offset printing. The printing properties of the said foils are caused by the fact that the light decomposition products of the diazo compounds are capable of accepting fatty inks, whereas the undecomposed diazo compounds are soluble in water and, in the presence of water, reject fatty inks.

As paper base there can be used known paper plates, especially those with a uniform surface, such as paper coated with a smooth mineral coating of mineral filler and adhesive, e. g. clay and casein. Parchmented papers can also be used.

As diazo compounds suitable for the new process there can be used diazo compounds of a higher molecular weight of the following general formula:

$$R—Y—Ar—N_2—X$$

wherein

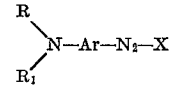
R means an aryl, aralkyl, a higher alkyl or an aroyl residue,
Y means O, S, NH or NR_1, R_1 standing for alkyl, aralkyl or aryl,
Ar means an aromatic residue, and
X an equivalent of an anion of an acid.

Under the term "aroyl" we understand the acyl radicals of aromatic carboxylic acids, e. g. benzoyl, and the expression "equivalent of an anion of an acid" is intended to designate radi-

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cals such as Cl', $SO_4''/2$, $ZnCl_4''/2$, $C_6H_5SO_3'$ and the like.

The substituent Y and the diazo group N_2 may preferably be in a para-position to each other. The aromatic residue Ar, the group R and the NH-group may contain further substituents. In the most cases it is advantageous, that the residues R and Ar are substituted by alkoxy, aroxy or N-aryl-sulfamido groups or by one or more halogen atoms. When using a diazo compound of the formula



as above defined the substituents R and R_1 can be connected with one another to form a cyclic compound, or R or R_1 can be connected with Ar by a covalent linkage, but it is not desirable to have sulfo groups as substituents in any of R, R_1 and Ar.

Another object of the present invention is the use of such diazo compounds which are obtained by treating the diazo compounds mentioned above with carbonyl compounds such as formaldehyde. Thus higher condensed diazo compounds are obtained which are rather valuable for the new process.

Another object of the present invention is the use of the so called diazo sulfonates which can be obtained by treating the diazo compounds with sulfites. A further object is the use of diazo-amino-compounds which can be obtained by causing the diazo compounds in question to react with guanidine, taurine or similar compounds, though the light sensitivity of these condensation products is usually weaker than that of the before mentioned products.

In the following, there are enumerated a lot of different diazo compounds suitable for the process of this invention, without limiting the scope. There are suitable the diazo compounds of 4-(N-benzyl-N-ethyl)-amino-aniline, 4-(N-2,6-dichloro-benzyl)-amino-aniline, 4-(N-cyclohexyl)-amino-aniline, 4-amino-2,5,4'-tribromo-diphenylamine, 4-amino-2',4',6'-trichloro-diphenylamine, 4-amino-2-[N-(2,5-diethoxy-phenyl)-sulfamido]-diphenylamine, 4-amino-3,6-dimethoxy-diphenylamine-2'-carboxylic acid, 1-amino-2,5-di-n-propoxy-4'-methyl-diphenylsulfide, N-(2,6-dichloro-benzyl)-3-amino-carbazol, 4-(N-2,3,4,6-tetrachloro-benzyl)-amino-aniline, 4-(N-2,6-dichloro-benzyl, N-ethyl)-amino-2,5-diethoxy-aniline, 4-amino-2,5,4'-triethoxy-diphenylether.

In order to provide the paper base with a layer of the light sensitive diazo compounds there can be used solutions or suspensions of the diazo compounds which are applied to the paper surface by coating, spraying, or by means of appliance-rollers or brushes or a pad. A surplus may be removed by doctor knives, by blowing with air, by flowing or by centrifuging. The coating solution shall have a neutral or weakly acidic reaction.

When using the sensitized paper foil for printing purposes, the foil is exposed to light under an original, where by the action of light the diazo compound is changed into an insoluble decomposition product. After the exposure, the printing foil can be developed by removing the undecomposed diazo compounds by washing with water or a solution of a salt. The foil, when wet, is treated with fatty ink which is accepted at those places having been met by the light during exposure. The foil is then brought into a suitable printing apparatus. It is possible to carry out the development and the treatment with fatty ink within the printing apparatus itself. It is possible to treat the foil after the exposure, that means in a dry state, at first with fatty ink and then with water or salt solutions, thereby removing the undecomposed parts of the diazo compounds with the parts of the fatty ink adhering to it, whereas the parts met by the light retain the fatty ink.

One other object of the present invention is the use of such paper foils which are laminated with plastic, metal or other paper foils. It is also possible to coat the back of the foil with water insoluble lacquers or to use intermediate layers of such lacquers.

Often paper printing foils of outstanding quality, in the first line of high resistance to water, can be prepared by incorporating the initial paper sheet with resins capable of being hardened, such as the well-known artificial resins representing condensation products of formaldehyde with phenol or urea or melamine.

An advantage may also be found in coating the base paper sheet with casein and/or mineral fillers, e. g. clay, with the purpose of smoothing the surface of the paper before applying the sensitizing solution.

In order to give the light sensitive paper foil a better stability during storing the layers containing the diazo compounds can include additions of products which make the diazo compounds difficultly soluble. For this purpose there may be used numerous inorganic salts and salts of sulfonic acids of the aliphatic or aromatic series. Simple tests will give the salts which are useful for any special diazo compound. Generally, the following salts will be suitable:

Cadmium-chloride, sodium-chloride, potassium-chloride, ammonium-chloride, zinc-chloride, sodium-sulfate, sodium salt of 2-butene-1,4-disulfonic acid, sodium salt of 2,5-dichlorobenzene-sulfonic acid, sodium salt of 4-chlorobenzene-sulfonic acid, sodium salt of 3,6-dichloro-5-nitrobenzene-sulfonic acid, sodium salt of 2,4-dinitro-toluol-6-sulfonic acid, sodium salt of 1-chloro-4-nitrobenzene-2-sulfonic acid, sodium salt of 4-oxy-benzene-sulfonic acid, sodium salt of 4,4'-dioxyl-diphenyl-2,2'-disulfonic acid, sodium salt of 1,5-naphthalene-disulfonic acid, sodium salt of 2-oxy-3-carboxy-naphthalene-6-sulfonic acid, sodium salt of 1,4-cyan-naphthalene-sulfonic acid, magnesium salt of 1,8-nitronaphthalene-sulfonic acid, sodium salt of 2,7-anthrachinone-disulfonic acid. These salts or an aqueous solution thereof are brought upon the paper foil before or after the coating of the solution of the diazo compounds.

The printing foils prepared with diazo-sulfonates or diazo-amino-compounds have good storing qualities.

A further object of this invention lies in a process of enhancing the storing qualities of the sensitized paper foils by adding to the coating solution additional diazo compounds or sulfonates of diazo compounds, which diazo compounds and sulfonates of diazo compounds must be stable in the dark and the light decomposition products of which are readily wettable by water and while so wet do not accept fatty inks. Such diazo compounds are f. i. alkoxy-diazo-compounds, such as the diazo compounds of p-anisidine, o-phenetidine, 4-amino-resorcinol-dimethylether, diazo-antipyrine. Merely as representatives of the above mentioned sulfonates of diazo compounds we wish to indicate the sulfonate of the diazo compound of aniline and that of p-toluidine, without restricting us thereto. A considerable enhancement of the storing quality of paper foils sensitized by means of f. i. the condensation product of 4-diazo-diphenylamine and formaldehyde is obtained by adding to the sensitizing solution the stabilizing diazo compound in a quantity of 10–100% with reference to the quantity of the said condensation product and using this solution for coating the paper foil. It is also possible to use both diazo compounds one after the other, but it is a considerable advantage to be able to apply both sensitizer and stabilizer in a single solution. When there are used stabilizing salts which have a precipitating action on the diazo sensitizer such stabilizers, of course, must generally be applied separately.

In order to get images which are clear and well visible immediately after the exposure to light, the light sensitive layer is advantageously intermingled with the diazo compounds of hydroxy-amino-carboxylic and sulfonic acids of the benzene and naphthalene series, in which the hydroxyl and amino group are standing in ortho-position to each other, such as the diazo compound of 3-amino-2-hydroxy-1-benzoic acid and 3 - amino - 4 - hydroxy - benzene - 1 - sulfonic acid. Such practice produces colored images.

Examples

(1) To a parchment paper sheet an aqueous solution containing 5% of the double salt of zinc chloride and the diazo compound obtained from 1 - amino - 2,5 - di - n - propyl - 4' - methyl-diphenylsulfide is applied and dried at a moderate temperature. After exposure to light under a negative (f. i. to the light of a carbon arc lamp), the paper sheet is clamped to an offset printing machine and washed with water by means of a sponge. Then printing ink and water are applied to the sheet in the usual manner. The printing machine is now ready for printing.

Instead of the above named diazo compound other diazo compounds, f. i. those cited in column 2, or mixtures of them may be used.

(2) A 3% aqueous solution of the sulfonate of the diazo compound of 4-amino-2',4',6'-trichloro-diphenylamine—the sulfonate can be manufactured as usual by reaction of the diazo compound with sodium sulfite—is brushed on parchment

paper being laminated together with a thin aluminum foil. When dry the thus formed light sensitive layer is exposed to light under a negative. The further proceeding is the same as described in Example 1 resulting in positive prints.

(3) An aqueous suspension of the guanidide of the diazo compound of 4-(N-2,6-dichlorobenzyl)-amino-aniline—the guanidide is to be prepared in the usual manner by acting upon the diazo compound with guanidine nitrate in a sodium carbonate solution—is spread by means of a cotton swab on a parchment paper foil being laminated with a thicker sheet of paper which on its backside has been coated with a water resistant lacquer. When dry the light sensitive layer is exposed to light under a negative all parts of the guanidide having been exposed to light being changed by the light influence to a material which takes up fatty inks. The foil is then clamped to an offset printing machine and the further proceeding is the same, as has been described in Example 1.

(4) A 2% aqueous solution of the condensation product formed from the diazo compound of 4-amino-diphenylamine by reaction with formaldehyde as described in U. S. patent specification 2,063,631 is spread on a paper printing foil by means of a cotton swab and the foil is dried. After having been exposed to light under a positive the foil is rubbed in with a fatty ink and subsequently developed with water containing some dextrin, the water being applied by means of a sponge. When used in an offset printing machine the paper printing foil produces negative prints.

(5) A paper printing foil is equally coated with a 2½% aqueous solution of the sulfonate of the diazo compound named in Example 4—the sulfonate is prepared by reaction of the diazo compound with sodium sulfite—and dried. The foil is then exposed to light under a negative, washed at first with water, subsequently with an aqueous solution containing in 100 parts by volume 2 parts by weight of mono-sodium phosphate and 1 part by weight of di-sodium phosphate, rinsed with water and clamped to a printing machine. The treatment of the foil with water and the phosphate solution may be effected after the foil has been clamped to the printing machine. Positive printings are produced.

(6) A paper printing foil is coated with a 6% aqueous solution of the double salt of zinc chloride and the diazo compound obtained from 4-(N-benzoyl)-amino-2,5-diethoxy-aniline. After having been dried the foil is exposed to light under a negative. The further proceeding is the same as has been described in Example 1. Positive prints are produced.

(7) After a paper printing foil has been coated with a 5% aqueous solution of cadmium chloride and has subsequently been dried, a 3% aqueous solution of the condensation product formed by reaction of 1 mol. 4-diazo-diphenylamine with 1 mol. formaldehyde as described in the U. S. patent specification 2,063,631 is applied to the foil. The foil is dried, exposed to light under a negative and further treated in the same way as indicated in Example 1. Positive prints are produced.

Printing foils having been pre-coated with cadmium chloride show a considerably better stability when not exposed to light than foils which have not been pre-coated in the same manner. Instead of cadmium chloride other salts, f. i. salts indicated in columns 3 and 4 of the specification may be used for the same purpose (pre-coating of the paper foil) and with similar effect, f. i. sodium chloride, zinc chloride, sodium sulfate, magnesium-1,8-nitro-naphthalene-sulfonate, sodium-1,5-naphthalene-disulfonate, sodium-chlorotoluol-sulfonate and many others. Likewise the stability of the light sensitive layers prepared with the aid of the other diazo compounds indicated above as proper substances (compare column 2 of the specification) can considerably be improved by pre-coating the printing foil with a solution of one of the heretofore described salts or mixtures thereof. The salts acting as stabilizers are characterized by the property of precipitating diazo compounds from water solution.

(8) The diazo compound of 4-amino-1,3-dimethoxy-benzene is brushed on a paper printing foil in the form of a 6% aqueous solution and subsequently dried. Then a 3% aqueous solution of the condensation product formed by reaction of 1 mol. of the diazo compound of 4-amino-diphenylamine with 1 mol. formaldehyde (compare U. S. patent specification 2,063,631) is brushed on the foil and dried. The foil is exposed to light under a negative and is then further treated as has been described in Example 4. When printing with a flat or offset printing machine positive prints are produced.

As good foils as are to be obtained by the above described two-stage process can be prepared by brushing on the paper printing foil a single aqueous solution containing both 2% 4-amino-1,3-dimethoxy-benzene and 3% of the formaldehyde condensation product of the diazo compound of 4-amino-diphenylamine and subsequently drying the foil.

Foils which have been prepared as heretofore described, can be stored for a much longer time when not exposed to light, than similar foils which have been manufactured without use of the diazo compound of 4-amino-1,3-dimethoxy-benzene or equivalent stabilizer. A similar good effect as to the improvement of the stability of the printing foils not exposed to light can be reached by using the diazo compounds of p-anisidine, o-anisidine, 4-amino-1-methylmercapto-3-methoxy-benzene, 4-amino-dimethylaniline, 1-amino-2-dimethylamino-4,5-(C-imino)-thiazol instead of the diazo compound of 4-amino-1,3-dimethoxy-benzene; they may f. i. be used in form of their zinc chloride double salts and their sulfonates respectively.

The condensation product of 4-diazo-diphenylamine and formaldehyde can be substituted by other diazo compounds, the decomposition products of which produced by light action take up fatty inks and representatives of which have been indicated in the specification and in the preceding examples. The stability of the light sensitive layer of the printing foils thus produced, if not exposed to light, is likewise considerably improved.

(9) An aqueous solution containing in 100 parts by volume 5 parts by weight of the diazo compound of 2-hydroxy-3-aminobenzoic acid and 5 parts by weight of the double salt of zinc chloride and the diazo compound of 4-amino-2',4',6'-trichloro-diphenylamine is brushed on a paper printing foil. The foil is dried and exposed to light under a negative. A good visible picture is produced, whereas the picture is more indistinct, if the diazo compound of 2-hydroxy-3-amino-benzoic acid is not incorporated into the light sensitive layer.

Other ortho-hydroxy-diazo compounds of the

benzene or naphthalene series, forming dyestuffs when being exposed to light, can be used instead of the diazo compound of 2-hydroxy-3-amino-benzoic acid, f. i. the diazo compounds of hydroxy-amino-benzoic acids and hydroxy-amino-naphthoic acids, the hydroxyl and amino groups standing in ortho position to each other. Furthermore hydroxy-amino-sulfonic acids of the benzene series, the hydroxyl and the amino groups being in ortho position to each other, may be used.

On the other hand the double salt of zinc chloride and the diazo compound of 4-amino-2',4',6'-trichloro-diphenylamine, in the above indicated combinations with ortho-hydroxy-diazo compounds, especially with the diazo compound of 2-hydroxy-3-amino-benzoic acid, can be substituted by the other diazo compounds and their sulfonates respectively having been described as sensitizers in the specification and the examples. Excellent printing foils are obtainable f. i. by using an aqueous solution containing in effective concentration the sulfonate of the formaldehyde condensation product of p-diazo-diphenylamine and the diazo compounds of 2-hydroxy-3-amino-benzoic acid and 4-hydroxy-3-amino-benzene-sulfonic acid respectively.

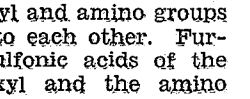
(10) A paper base which is very satisfactory for the use of our present invention is a rosin-sized paper having wet-strength properties derived from inclusion in the furnish of melamine-formaldehyde resin and weighing about 25 pounds per thousand square feet, coated on at least one side with about 5 pounds dry weight, per thousand square feet of surface coated, of a coating composition comprising clay 100 parts, ammonium caseinate 18 parts and dimethylol urea 1½ parts. The paper after being dried is smoothed by means of a supercalender and may advantageously, but not necessarily, be further treated by brushing with a bristle brush according to the disclosure of Italian Patent No. 434,094.

This paper base is equally coated with a 2½% aqueous solution of the sulfonate of the diazo compound being formed by condensing 1 mol. of the diazo compound of 4-amino-diphenylamine with 1 mol. of paraformaldehyde in sulfuric acid of 60° Bé. (see Example 4)—the sulfonate is prepared by reaction of the diazo compound with sodium sulfite—and dried. It is adapted for being further treated as has been described in Example 5.

It is understood that in the following claims the terms alkyl, aralkyl, aryl and aroyl (= acyl radical of an aromatic carboxylic acid) include residues bearing one or several substituents as may be seen from the numerous representatives of diazo compounds enumerated in the description and in the examples.

What we claim is:

1. A photosensitive coated paper product suitable for the photolithographic manufacture of greasy ink receptive planographic printing plates which product comprises a paper base, selected from the group consisting of parchmented papers and papers coated with a coating composition comprising mineral filler and adhesive, which paper base has a uniform surface having planographic printing properties, and a top coating thereon free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, said coating comprising a diazo compound which on exposure to actinic light yields an oleophilic decomposition product and is selected from the group consisting of sulfonates obtained by reaction of a sulfite upon compounds selected from the group consisting of (1) the diazenium salts corresponding to the formula



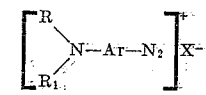
wherein X stands for an equivalent of an anion of an acid, Ar stands for an aromatic residue selected from the group consisting of phenylene and phenylene substituted by a member of the group consisting of alkyl, alkoxy, aroxy, arylsulfamido and halogen, R stands for a member of the group consisting of aryl, and its alkyl, alkoxy, halogen and carboxyl substitution products, and R_1 stands for a member of the group consisting of H and alkyl, and (2) the condensates of (1) with aldehydes.

2. The product defined in claim 1, in which Ar stands for phenylene and R stands for aryl.

3. A photosensitive coated paper product suitable for the photolithographic manufacture of greasy ink receptive planographic printing plates which product comprises a paper base, selected from the group consisting of parchmented paper and papers coated with a coating composition comprising mineral filler and adhesive, which paper base has a uniform surface having planographic printing properties, and a top coating thereon free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, said coating comprising the diazo sulfonate obtained by reaction of a sulfite upon an aldehyde condensate of a paradiazonium salt of a diphenylamine, said diazo sulfonate being capable of yielding an oleophillic decomposition product on exposure to actinic light.

4. The product defined in claim 3 in which the aldehyde is formaldehyde.

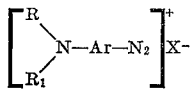
5. A photosensitive coated paper product adapted for use for greasy ink receptive photolithographic printing plates which comprises a paper base, on one surface of the paper base a hydrophilic coating of mineral coating composition comprising finely divided mineral filler and adhesive, the surface of said coating being uniform and having planographic printing properties, and over the mineral coating a light-sensitive layer free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, said light-sensitive layer comprising a sulfonate obtained by reaction of a sulfite upon a condensate of an aldehyde and a diazonium salt having the formula



wherein X stands for an equivalent of an anion of an acid, Ar stands for an aromatic residue selected from the group consisting of phenylene and phenylene substituted by a member of the group consisting of alkyl, alkoxy, aroxy, arylsulfamido and halogen, R stands for a member of the group consisting of aryl and its alkyl, alkoxy, halogen and carboxyl substitution products, and R_1 stands for a member of the group consisting of H and alkyl, said sulfonate yielding an oleophilic decomposition product on exposure to actinic light.

6. The process of manufacturing printing

plates for use in lithography which comprises the steps of forming a light-sensitive layer by coating paper, selected from the group consisting of parchmented papers and papers coated with a coating composition comprising mineral filler and adhesive a surface of which is uniform and has planographic printing properties, with a diazo compound in aqueous medium which is free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, the diazo compound being selected from the group consisting of (1) the diazonium salts corresponding to the formula

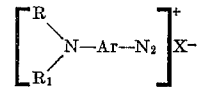


wherein X stands for an equivalent of an anion of acid, Ar stands for an aromatic residue selected from the group consisting of phenylene and phenylene substituted by a member of the group consisting of alkyl, alkoxy, aroxy, arylsulfamido and halogen, R stands for a member of the group consisting of aryl and its alkyl, halogen and carboxyl substitution products, R_1 stands for a member of the group consisting of H and alkyl (2) the condensates of (1) with aldehydes, and (3) the diazo sulfonates obtained by reaction of sulfite upon (1) and (2), drying the coated paper, forming an oleophilic image in the light-sensitive layer by exposing it to light under an original, washing off the unexposed parts of the layer with an aqueous liquid and applying greasy ink and an aqueous liquid to the layer side of the paper sheet.

7. The process of manufacturing printing plates for use in lithography which comprises the steps of forming a light-sensitive layer by coating paper, selected from the group consisting of parchmented papers and papers coated with a coating composition, comprising mineral filler and adhesive, a surface of which is uniform and has planographic printing properties with a diazo sulfonate, obtained by reaction of a sulffite upon an aldehyde condensate of a paradiazonium salt of a diphenylamine, in an aqueous medium which is free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, drying the coated paper, forming an oleophilic image in the light-sensitive layer by exposing it to light under an original, washing off the unexposed parts of the layer with an aqueous liquid and applying greasy ink and an aqueous liquid to the layer side of the paper sheet.

8. The process as defined in claim 7 in which the aldehyde is formaldehyde.

9. The process of of manufacturing printing plates for use in lithography which comprises first providing a paper sheet with a uniform surface having planographic printing properties by precoating the paper sheet with a coating composition comprising a finely divided mineral filler and an adhesive and drying the coated paper, then applying to the precoated paper a diazo sulfonate obtained by reaction of a sulfite upon an aldehyde condensate of a diazonium salt corresponding to the general formula



wherein X stands for an equivalent of an anion of an acid, Ar stands for an aromatic residue selected from the group consisting of phenylene and phenylene substituted by a member of the group consisting of alkyl, alkoxy, aroxy, arylsulfamido and halogen, R stands for a member of the group consisting of aryl and its alkyl, alkoxy, halogen and carboxyl substitution products, and R_1 stands for a member of the group consisting of H and alkyl, in aqueous medium which is free from coupling components and free from colloidal substances tannable by diazo compounds under the action of actinic light, drying again the coated paper, forming an oleophilic image in the light-sensitive layer by exposing it to light under an original, washing off the unexposed parts of the layer with an aqueous liquid and applying greasy ink and an aqueous liquid to the layer side of the paper sheet.

10. The process as defined in claim 9 in which Ar stands for phenylene, R stands for phenyl and R_1 stands for hydrogen.

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