Patented Oct. 26, 1954

2,692,827

UNITED STATES PATENT OFFICE

2,692,827

PROCESS OF DEVELOPING PHOTOLITHOGRAPHIC PRINTING PLATES

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No Drawing. Application April 23, 1951, Serial No. 222,523

8 Claims. (Cl. 95—5.4)

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In the practice of photolithography a suitable base such as a grained metal plate or a suitably prepared (e. g., mineral-coated) paper sheet having a hydrophilic surface and bearing a water-soluble photosensitive coating which becomes water-insoluble and more or less hydrophobic upon exposure to actinic radiation is imaged by exposure to actinic radiation and is then developed. The development serves to remove or wash off the unexposed areas of the photosensitive coating and to leave such areas wet with water and repellent to ink and to leave the exposed areas or image repellent to water and wettable by ink. Exposed photosensitive plates have been developed heretofore generally by one or the other of the following methods depending upon the character of the plate.

(*a*) The exposed plate may be first coated with developing ink and then scrubbed with water to remove the unexposed areas of the photosensitive coating together with the ink adhering thereto and to leave such areas wet with water, the exposed areas with the adhering ink remaining unaffected by the scrubbing treatment. The so-developed plate may then be printed by being contacted successively with a wetting roller, an inking roller and the surface to be printed. In the printing process the inked imaged areas will continue to take ink from the inking roller and to repel water and the wetted unimaged areas will continue to take water from the wetting roller and to repel ink. This is the customary procedure with plates having the conventional photosensitive layer of albumin and ammonium bichromate.

(*b*) The exposed plate is simply washed with water to remove the unexposed areas of the photosensitive coating and then put into the printing machine where it is contacted successively with a wetting roller, an inking roller and the surface to be printed. In this process the plate may be somewhat slow to take ink on the imaged areas so that good prints will not be produced immediately and possibly not until after the machine has run for a considerable length of time during which a number of defective prints will have been made.

The albumin-dichromate plates are short lived and must be freshly prepared within a few hours before they are used. Besides the developing process described is time-consuming.

Recently photosensitized planographic printing plates have appeared on the market comprising a base of coated paper or other material and bearing on the surface a photosensitive layer composed of a high molecular weight water-soluble diazo compound which will become insoluble under the action of actinic radiation. An important advantage possessed by such plates in comparison with conventional albumin plates is that they have a comparatively long shelf-life, so that they can be purchased in sensitized condition by the ultimate user and stored for a considerable time before actual use. The length of time plates of this type can be stored without apparent deterioration may vary from a few weeks to more than a year, depending upon the particular diazo compound used as sensitizer.

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In some cases, and especially in the case of plates capable of long storage, it happens that the plate after exposure and washing with water may be slow to take ink on the imaged areas.

It appears that when the exposed plate is developed by method (*b*) the exposed areas become to some extent wet with water and as a result repel ink until the water gradually is replaced by ink.

The method commoly used for the development of the albumin-bichromate plates is not suitable for the development of the diazo plates for the following reason. The albumin - dichromate coating is relatively thick amounting to one pound or more per 1,000 square feet of surface so that the developing ink applied to the exposed plate does not penetrate through the coating to the supporting base and is entirely removed from the unimaged areas by the scrubbing with water leaving the unimaged areas clean. In the diazo plates, on the other hand, the coating is relatively thin amounting to only from one to several ounces per 1,000 square feet. Consequently, if a conventional developing ink is applied to the exposed plate it will penetrate through the coating to the supporting base and will not be cleanly removed from the unexposed areas by scrubbing with water. As a result both the exposed and the unexposed areas will take ink and give defective prints.

The object of my invention therefore is to provide a method for the development of plates having diazo photosensitive coatings, which method shall avoid the objectionable features of the prior development methods referred to above and will render the imaged areas of the plate immediately wettable by ink while leaving the unimaged areas clean and receptive to water and consequently repellent to ink.

As diazo compounds suitable for the new process there can be used diazo compounds of a

higher molecular weight of the following general formula

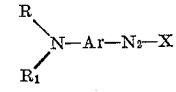
$$R—Y—Ar—N_2—X$$

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" I 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 radicals 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 most cases it is advantageous if 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.

Diazo compounds which are obtained by treating the diazo compounds mentioned above with carbonyl compounds such as formaldehyde may be used. Thus higher condensed diazo compounds are obtained which are especially valuable for the new process.

The so-called diazo sulfonates which can be obtained by treating the diazo compounds or the aldehyde-diazo compound reaction products with alkali metal sulfites also may be used. Further diazo-amino-compounds which can be obtained by causing the diazo compounds in question to react with guanidine, taurine or similar compounds may be used. The light sensitivity of these condensation products is usually weaker than that of the before-mentioned products and the shelf-life of plates coated therewith is correspondingly longer.

Typical diazo compounds which when applied to paper and exposed to actinic radiation yield images which are benefited by treatment according to the invention include the diazo compounds of 4 - (N - benzyl - N - ethyl) - amino - aniline, 4 - (N - 2,6 - dichlorobenzyl) - amino-aniline, 4-(N-cyclohexyl)-amino-aniline, 4-amino-2,5,4'-tribromo - diphenylamine, 4 - amino-2',4',6'-trichlorodiphenylamine, 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 - tetrachlorobenzyl) - amino - aniline, 4 - (N - 2,6 - dichlorobenzyl, N-ethyl)-amino-2,5-diethoxy-aniline and 4-amino-2,5,4'-triethoxy diphenyl-ether.

My invention is applicable to any diazo image which is not sufficiently water-repellent but is more particularly adapted for use with diazo images derived from the sulfonates formed by

reacting an alkali metal sulfite, e. g. sodium sulfite, with the reaction products of aldehydes such as formaldehyde with diazo compounds of the type defined above, said sulfonates generally giving plates having a relatively long shelf-life but yielding images which tend to be deficient in water-repellence.

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 should have a neutral or weakly acidic reaction.

In practicing my present invention, I provide a suitable base, such as a coated paper base and preferably a water-impervious paper base, with a thin photosensitive layer of diazo-compound of the type previously mentioned; I expose the sensitized surface through a transparency to the action of actinic radiation; I treat the exposed surface with non-penetrating, hydrophobic, olephilic material and thereby render the exposed or imaged areas water-repellent; and I wash the entire surface with aqueous liquid to clean the unexposed areas and provide a plate ready for use as a printing plate on a planographic printing press or rotary offset duplicator.

The non-penetrating, hydrophobic material used to promote water-repellency of the imaged areas may be (1) a finely divided powder or dust, such as finely powdered heavy metal soap or non-water-absorbent dyestuff; or it may be (2) an oily material of at least medium viscosity, such as oleic acid; or advantageously it may be a solution or suspension of (1) in (2).

Typical metal soaps suitable for use according to the invention include zinc stearate, aluminum palmitate, calcium oleate, and the like. Typical hydrophobic dyestuffs include Oil Red, Oil Orange, Hansa Yellow, and the like. Water-shedding powdered material of the type indicated may be applied to the surface of an exposed plate by means of a soft brush or a pledget of cotton. It is found that hydrophobic powder so applied adheres firmly to the exposed or imaged areas of the plate. When the so-treated plate is subsequently washed or wiped with a sponge dampened or wet with water, the unexposed areas are easily wiped clean of both the still soluble unexposed diazo-sulfonate sensitizer and any overlying water-repellent powder which may be adhering thereto. It will be noted that during the cleaning or washing operation the image areas, to which the water-repellent powder particles adhere, are not wet by the wash water because the water is repelled by the said water-repellent or water-shedding particles. Likewise the image is not wet by subsequently applied aqueous lithographic wet-out or dampening solution. Consequently when the plate is put on an offset printing press the image is still dry and in condition to pick up ink upon first contact with the inking-rolls, thus avoiding loss of time hitherto required for ink to displace water on untreated images which have adsorbed water or aqueous lithographic solution.

Alternatively, instead of a water-repellent powder, there may be used a non-penetrating, water-repellent, oily liquid, such as oleic acid, any of various vegetable oils having viscosities approximating that of oleic acid or liquid sili-

cones having viscosities at least as high as that of oleic acid. In fact, oxidized or polymerized turpentine, if sufficiently viscous, can be used successfully. However, in the use of the latter substance care must be taken that the oxidation or polymerization has proceeded far enough that the material will not penetrate through the diazo-sulfonate coating to contaminate the underlying base. To treat the plate with the hydrophobic liquid a swab wet with oleic acid or similar oily material is wiped over the exposed surface of the plate, whereby the imaged areas are wet by the said oily material and consequently are rendered non-water-wettable. When the surface is subsequently wiped with a sponge wet with water the unexposed, still soluble sensitizer is removed together with any overlying film of oily material whereas the insoluble, imaged areas remain with a film of the water-repellent, oily material thereon. Thereafter it is found that the oil-treated image immediately picks up ink from an inking-roll passed thereover, so that prints can be made therefrom without delay. In place of the oleic acid mentioned there may be substituted with very similar results olive oil, cotton-seed oil, rapeseed oil, peanut oil, or the like.

It is frequently found advantageous to dissolve an oil-soluble dyestuff in the oleic acid or other oil used according to the invention. The resulting solution makes the image on the plate more readily visible before it is inked, and probably likewise makes it slightly more water-repellent. Such dyestuffs are usually only sparingly soluble in oleic acid or vegetable oils, and may in general be added up to the limit of their solubility. Alternatively or in conjunction, small quantities of water-insoluble metallic soap may be dissolved in the hydrophobic oily material, thereby increasing the viscosity and decreasing the penetrating qualities thereof, as well as increasing to some extent the water-repellency of the image treated therewith. The useful quantity of metal soap to be dissolved in the oleic acid or other oil in general falls within the range of from 0.1 to 5 percent of the weight of solvent. For example, solutions of 0.25 percent of aluminum oleate, 1.0 percent of zinc oleate, and 2.5 percent of magnesium oleate have all given good results. Stearates and palmitates may be used in place of oleate soaps if desired.

Example 1

In a typical case a planographic printing plate was used which comprised a water-impervious paper base provided by a suitable water-barrier coating and having on one side a super-calendered coating of casein and clay in amount of about 2½ pounds, dry weight, per 1000 square feet of surface and a thin overlying layer, amounting to about 1.1 ounces, dry weight, per 1000 square feet of the water-soluble sulfonate formed by reacting sodium sulfite and the zinc double salt of the reaction product of formaldehyde and 4-diazo-1,1' diphenylamine (see U. S. Patent No. 2,063,631). This plate was exposed through a negative transparency to the action of actinic radiation, whereby the exposed areas of the diazo-sulfonate product were rendered insoluble in water but did not become unwettable by water. The exposed surface was wiped over with a cotton swab moistened with oleic acid. Next the surface was swabbed with a pad moistened with water which removed from the unexposed areas the still soluble photosensitive material together with any overlying oleic acid. The surface was then wiped over with a swab wet with a standard lithographic starting solution ("Platex" manufactured by the Addressograph-Multigraph Corporation of Cleveland, Ohio). Thereafter the plate was immediately placed in a rotary offset duplicator where the plate at once satisfactorily picked up ink on the imaged areas, and at once gave satisfactory black prints therefrom.

Similar results are obtainable by substituting the following for the oleic acid of the foregoing example:

a. Powdered aluminum stearate.
b. Powdered Oil Red (Color Index No. 258).
c. Powdered Hansa Yellow (a lake) suspended in olive oil.
d. General Electric Company's Silicone Oil 9981 LT70NV.
e. Polymerized turpentine.
f. Cottonseed oil.
g. Oil Orange (Color Index No. 24) dissolved in oleic acid.
h. Oleic acid containing 2% of dissolved magnesium oleate.

Example 2

The supercalendered clay-coated paper base of Example 1 was washed with a 3 per cent aqueous solution of the sulfonate formed by reacting sodium sulfite in aqueous solution with the diazo compound of 4-amino-2',4',6'-trichloro-diphenylamine. The product was dried at moderate temperature and exposed through a negative to actinic radiation. The surface was wiped over with a cotton swab moistened with oleic acid. Then the surface was swabbed with a pad moistened with water, which removed from the unexposed areas the still soluble photosensitive material together with any overlying oleic acid. The surface was then wiped over with a swab wet with a standard lithographic starting solution ("Platex") and the plate was placed in a rotary offset duplicator where the imaged areas at once satisfactorily picked up ink, while the background remained satisfactorily clean.

Example 3

A supercalendered clay-coated paper similar to that used in Example 1 was coated with about 3 oz. dry weight, per thousand square feet, of the guanidide of the diazo compound of 4-(N-2,6-dichloro-benzyl)-amino-aniline deposited from aqueous medium. The sheet was dried at moderate temperature and exposed through a negative to radiation from an arc-lamp. The surface was then wiped with a swab moistened with oleis acid, and was then washed with water. The resulting plate was then wet with a standard lithographic starting solution ("Platex") and run in a rotary offset duplicator where the imaged areas immediately took up ink satisfactorily while the unimaged areas remained satisfactorily clean.

I claim:

1. Process which comprises exposing to actinic radiation a paper base having a surface sensitized with a coating of a photosensitive composition comprising a member of the group consisting of diazo compounds of the general formula R—Y—Ar—N_2—X wherein R stands for a member of the group consisting of alkyl, aralkyl, aryl and aroyl, Y stands for a member of the group consisting of O, S, NH, N-alkyl, N-aralkyl and N-aryl, Ar stands for aryl and X stands for an equivalent of an anion of an acid, the amino derivatives of said diazo compounds, the sulfonates of said diazo compounds, the reaction products of said diazo compounds and carbonyl compounds and the sulfonates of said reaction prod-

ucts of said diazo compounds and carbonyl compounds; treating the exposed surface with a non-penetrating substance from the group consisting of powdered water-insoluble metal soaps, powdered water-repellent dyestuffs, oleic acid, vegetable oils, liquid silicones of viscosity as high as that of oleic acid, and turpentine polymerized to a high viscosity; washing the surface with water; and printing copies from the treated surface by the offset printing process.

2. Process as defined in claim 1 in which the composition comprises a sulfonate of the diazo compound.

3. Process as defined in claim 1 in which the composition comprises a reaction product of an aldehyde and the diazo compound.

4. Process as defined in claim 1 in which the composition comprises the sulfonate of a reaction product of an aldehyde and the diazo compound.

5. Process as defined in claim 1 in which the composition comprises an amino derivative of the diazo compound.

6. Process as defined in claim 1 in which the composition comprises the guanidide of the diazo compound of 4-(N-2,6-dichloro-benzyl)-amino-aniline.

7. Process as defined in claim 1 in which the composition comprises the reaction product of sodium sulfite and the diazo compound of 4-amino-2',4',6'-trichloro-diphenylamine.

8. Process which comprises exposing to actinic radiation the surface of a planographic printing plate having a paper base which is sensitized by a photosensitive composition formed by reacting an alkali metal sulfite with the zinc double salt of the formaldehyde condensation product of 4-diazo-1,1'-diphenylamine, moistening the exposed surface with oleic acid, thereafter washing the treated surface with water, and applying aqueous lithographic-solution and lithographic printing-ink to the surface.

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