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3,756,823

PLANOGRAPHIC DIAZO PRINTING PLATE

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16 Claims

ABSTRACT OF THE DISCLOSURE

A paper-based planographic printing plate giving up to 1500 or more good prints with reproduction of fine screen areas is obtained by providing a water-repellent coating on the paper surface, on that coating an intermediate layer of a filler-permeated mixture of a hydrophilic organic binder and a hydrophobic thermoplastic film-forming polymer, on that layer a filler-permeated planographic layer of cross-linked polyvinyl alcohol having a degree of hydrolysis greater than 98% and a light-sensitive diazo compound coated on the planographic layer. The intermediate layer is formed from an aqueous dispersion of hydrophobic polymer and filler, advantageously finely divided clay, having the hydrophilic binder, e.g., a starch derivative, and a crosslinking agent in the continuous phase. The filler in the planographic layer advantageously is pigmentary TiO_2 . The light-sensitive coating is formed into a water-insoluble ink-receptive image by imagewise exposure and development with an azo coupling component, giving a positive image, in use of a diazonium salt of high coupling activity, e.g., a 4-benzoylamino-2,5-dialkoxy benzene diazonium salt, and by imagewise exposure giving a negative image when a diazo resin is used.

This invention relates to a planographic printing plate sensitized with a diazo compound, which plate consists of a paper base having coated thereon in succession a water-repellent layer, an intermediate layer, and a planographic layer the surface of which is sensitized with a diazo compound. The invention relates further to a process of producing the planographic printing plates.

In the art of planographic printing, of which offset printing is the most prominent form, plates of paper are used on a fairly large scale for producing limited numbers of prints. In its simplest form the paper planographic printing plate consists of a paper base and a planographic layer. With these simple one-layer plates it is possible to run off a few hundred of prints. If a few thousands of prints are desired, the paper base must be protected against the action of the (aqueous) fountain solution with which the planographic printing plate is constantly wetted during the printing process. This protection is usually ensured by providing one or more water-repellent layers between the base, which is preferably a so-called wet-strength paper, and the planographic layer. As the highly hydrophilic planographic layers are commonly applied from aqueous liquids, they tend to have poor adhesion to the water-repellent layers. For this reason one or more adhesive layers are also provided between the water-repellent layer(s) and the planographic layer.

The planographic layer of a paper planographic printing plate consists as a rule of water insoluble or insolubilized hydrophilic binder and one or more fillers. In the literature many suggestions for the composition of a planographic layer are to be found. The binders mentioned include: gelatine, casein, zein, soya bean protein,

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albumin, animal glue, hydroxyethyl cellulose, sulphoethyl cellulose, carboxymethyl cellulose, cellulose sulphate, methyl cellulose, oxidized cellulose, carboxymethylhydroxyethyl cellulose, methylethyl cellulose, starch, hydroxyethyl starch, glucosan, glucosan-2-monocarbamate, oxidized starch, starch acetate, enzyme converted starch, acid-modified starch, chlorinated starch, starch glycolate, reaction products of hydroxyethyl starch with aminoformaldehyde resins, pectin derivatives, alginic acid, gum arabic, Irish moss, chitosan, dextrin, dextran, locust bean gum, adragant gum, mesquite gum, karaya gum, guar gum, polyvinyl alcohol, polyacrylic acid, polyacryl amides, methylolpolyacryl amide, polyamides and copolymers of acrylic acid, methacrylic acid, and their amides with hydrophobic monomers such as styrene, vinyl acetate, or ethyl acrylate.

The fillers proposed include: zinc oxide, titanium dioxide, barium sulphate, antimony trioxide, carbon-black, calcium carbonate, magnesium carbonate, lithopone, aluminium oxide, calcium fluoride, magnesium oxide, calcium oxide, silica, kaolin, bentonite, aluminium silicate, diatomaceous earth, satin white, talc, fuller's earth, Georgian clay or calcined clay.

Familiar water-repellent layers consist, for instance, of urea, phenol, and melamine-formaldehyde resins, vinyl resins, alkyd resins, polyester resins, polyacrylates, polymethacrylates, neoprene, rubber hydrochloride, chlorinated rubber, nylon, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, polyvinylbutyral, copolymers of an unsaturated dicarboxylic acid with styrene, of styrene with butadiene, of butadiene with acrylonitrile. The water-repellent layer may contain one or more fillers.

Anchoring layers for anchoring a planographic layer to a subjacent water-repellent layer consist almost invariably of a protein, specifically casein, and a filler. The protein is insolubilized with the aid of a cross-linking agent such as dimethylolurea.

In the light-sensitive paper planographic printing plates a light-sensitive substance is present on the surface of the planographic layer. These plates are either positive-acting or negative-acting. If such plates are intended for printing more than 1000 prints, high demands are made as to the quality of the prints made with them. Besides, these plates must be suitable both for printing so-called line drawings as well as for printing fine screen areas (half-tone screen images).

For the sensitization of the negative-acting plates so-called diazo resins are commonly used. These diazo resins are produced by condensing specific aromatic diazo compounds, such as p-diazodiphenylamine or a derivative thereof, in a strongly acidic medium with an aldehyde or a ketone, usually with formaldehyde. They are water-soluble, but decompose upon exposure into water-insoluble yellow-brown-toned products which are receptive for printing ink. The plates sensitized with diazo resin are converted into a printing form by exposing their light-sensitive layer imagewise under a negative original and subsequently washing away the unexposed diazo resin with an aqueous liquid.

Positive-acting paper planographic plates can be sensitized with an actively coupling non-polymeric benzene diazonium compound forming a hydrophilic photodecomposition product (or at least a photo-decomposition product which does not accept printing ink). These plates are converted into a printing form by developing them, after imagewise exposure under a positive original, with a liquid containing an azo component. Such positive-acting paper planographic printing plates are well known.

United States patent application Ser. No. 790,174, now Pat. No. 3,658,538, which was filed on Jan. 9, 1969 and copending herewith, describes a positive-acting planographic printing plate in which the base is coated directly with a planographic layer containing polyvinyl alcohol having a high degree of hydrolysis and a filler. The planographic layer is sensitized with a benzene diazonium salt. This very simple planographic printing plate is suitable for printing line-drawings in small numbers. Fine screen areas, however, are not reproduced by this plate in the quality desired by the printer. Moreover, in fine screen areas the plate tends to break up very readily, so that only small numbers of prints can be printed from screen images.

British patent specification 1,064,129 describes a light-sensitive paper planographic printing plate having a paper base, which is coated on one side with a superficially saponified cellulose acetate layer (anchored to the base with the aid of an adhesive layer) and with a planographic layer containing hydroxy-ethyl cellulose, cross-linked with glyoxal, and titanium dioxide. The planographic layer is sensitized with a benzene diazonium salt. With this planographic printing plate, prints of sufficiently high quality are obtained. However, the plate is not entirely satisfactory because (a) its composition is much too expensive and (b) the mutual adhesion of the various layers leaves much to be desired, so that the number of copies obtainable is too small. Frequently it has not been found possible with such a plate to produce as many as 1500 prints.

It is an object of the present invention to provide a light-sensitive paper-based planographic printing plate which yields up to 1500 or more prints of sufficiently high quality and reproduces fine screen areas satisfactorily, and which is made to be either positive-acting or negative-acting as desired.

The planographic printing plate according to the invention consists of a paper base coated on at least one side with successively a water-repellent layer, an intermediate layer, and a planographic layer sensitized with a diazo compound, the intermediate layer containing a hydrophobic thermoplastic film-forming polymer, a hydrophilic binder, and a filler, and the planographic layer containing cross-linked polyvinyl alcohol having a degree of hydrolysis exceeding 98%, and one or more fillers.

It has been found that such a planographic layer is distinguished by an excellent water retaining ability and a low toning tendency and by good sensitizability with aqueous solutions of benzene diazonium compounds. The polyvinyl alcohol can be cross-linked with known agents. Good results are obtained, inter alia, with glyoxal and formaldehyde. The filler to be used in the planographic layer may, for instance, be zinc oxide, titanium dioxide, barium sulphate, antimony trioxide, calcium carbonate, lithopone, aluminum oxide, calcium oxide, silica, kaolin, bentonite, aluminum silicate, diatomaceous earth, clays, or mixtures of such fillers. The planographic layer preferably contains titanium dioxide having an average particle size of about 200 m μ as filler, for with this filler an optimum reproduction of details is obtained even in very fine screen areas. If desired, the planographic layer may contain mixtures of fillers. A suitable mixture, for instance, is one of a filler with a fairly large (150 nm.) and a filler with a fairly small (80 nm.) particle size. The planographic layer is applied on the intermediate layer with the aid of an aqueous liquid which contains polyvinyl alcohol having a degree of hydrolysis exceeding 98% and a cross-linking agent in the continuous phase and a filler in the dispersed phase. The polyvinyl alcohol is cross-linked by heating.

Between the planographic layer and the water-repellent layer a special intermediate layer is provided. The object of this intermediate layer is to level the surface and to ensure good adhesion of the planographic layer. Leveling is necessary to make possible the application of a planographic layer with a sufficiently smooth surface, which is necessary to obtain a good reproduction of details, even

of very fine screen areas. In addition to a filler, the intermediate layer contains a thermoplastic hydrophobic film-forming polymer (hereinafter briefly referred to as the polymer) and a hydrophilic binder. It is preferably applied on the water-repellent layer with the aid of an aqueous dispersion containing a filler and the polymer in the dispersed phase and a hydrophilic binder in the continuous phase.

The polymer is a water-dispersible product which is capable of film-forming at temperatures between 90 and 160° C. (the temperature at which the layer is dried) and adheres satisfactorily to the water-repellent layer. To ensure rapid-film-forming, the polymer is preferably chosen to have a softening temperature below 110° C. Aqueous dispersions of thermoplastic film-forming polymers with a softening temperature below 110° C., hereinafter called latices, are commercially available. These latices can be used as such in the aqueous coating liquid with the aid of which the intermediate layer is formed. Good results are obtained with latices of polyvinyl esters such as polyvinyl acetate, polyvinyl chloride, and polyvinyl acetate-chloride, of polyacrylic ester such as polyethyl acrylate, of polymethacrylic esters such as polymethyl methacrylate and poly-n-butyl methacrylate, and of elastomers on a butadiene basis such as the copolymers of butadiene with styrene and/or acrylonitrile.

The choice of the hydrophilic binder for the intermediate layer is not very critical. Preferably a binder forming low-viscosity solutions is chosen.

Particularly attractive binders are polyvinyl pyrrolidone and starch derivatives such as hydrolyzed starch, oxidized starch, dextrin, hydroxyethyl starch, starch acetate (having a low acetyl content), and enzyme converted starch.

Nevertheless use can also be made of binders which dissolve in water while forming more viscous solutions (e.g. polyvinyl alcohol, casein, cellulose derivatives, alginates, gum arabic). The hydrophilic binder is insolubilized with the aid of a cross-linking agent, e.g. formaldehyde or glyoxal. Examples of the filler which the intermediate layer may contain are clays, e.g. kaolin, titanium dioxide, calcium carbonate, barium sulphate, satin white, talc, or mixtures of such fillers. Preferably clay is used, e.g. China clay, Columbia coating clay, because very smooth surfaces are obtained with them.

The weight ratio hydrophilic binder/polymer varies between 0.2 and 1, preferably between 0.3 and 0.7.

The weight ratio between the filler and the quantity of the mixture of polymer plus hydrophilic binder varies preferably between 3 and 7. The intermediate layer has a dry weight of 7–15 g./m.².

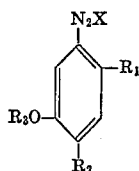
The familiar water-repellent layers for paper planographic printing plates may be used as water-repellent layers. The water-repellent layer must prevent water absorption by the paper base and should absorb only a small amount of moisture. On the other hand this layer must be receptive to aqueous coating liquids. Very suitable water-repellent layers consist of, besides a filler, a combination of a thermosetting hydrophobic polymer (such as a urea- or melamine-formaldehyde resin) and a thermoplastic hydrophobic polymer or an elastomer. The dry weight of the water-repellent layer is preferably of the order of magnitude of 8–15 g./m.².

Any type of paper known for use for the production of paper planographic printing plates can be used as the support. The support is preferably highly satinated paper of weight 110–140 g./m.².

The planographic layer is sensitized with a very actively coupling benzene diazonium salt. By very actively coupling benzene diazonium compounds are here to be understood benzene diazonium compounds which have greater coupling activity than 1-diazo-4-N-methyl-N-cyclohexyl-amino-3-chlorobenzene. A method for determining the coupling activity of diazonium compounds is described in British patent specification 957,836. More particularly suitable diazonium compounds for sensitization of the

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planographic layer are those satisfying the general formula:



in which X is an anion, R₁ is an alkoxy or a



group in which R₄ is an alkyl, cycloalkyl or aralkyl group and COR₅ is an acyl group, R₂ is an acylamino or an etherified mercapto group, and R₃ is an alkyl group.

Diazonium compounds satisfying this formula are described, inter alia, in U.S. Pats. 3,311,475 and 3,338,713, British patent specifications 347,430 and 1,045,242, Dutch patent specification 51,536, and French patent specification 1,406,166.

Stabilizers known for use in the diazotype process may be included in the sensitizing liquid. Good stabilization is obtained with a mixture of a major proportion, e.g., 5 parts, of boric acid and a minor proportion, e.g., 1 part, of tartaric acid.

The positive-acting light-sensitive plate is developed, after imagewise exposure under a positive original, for the purpose of forming the oleophilic azo dyestuff image, with an aqueous buffered solution of phloroglucinol having a pH between 6 and 7. The buffering of the developer can be effected with the buffer salts commonly used for diazo-type developers. Good results are obtained with phosphate buffers. Immediately after the development the printing form is ready.

Instead of being sensitized with a benzene diazonium salt, the planographic printing plate according to the invention can be sensitized with a diazo resin. In that case a negative-acting planographic printing plate having very attractive properties is obtained. It is a considerable advantage of this negative-acting plate that it can be developed with ordinary water to a printing form ready for printing. Indeed the unexposed diazo resin can be almost completely removed from the planographic surface with water. Very little diazo resin remains behind on the plate and it does not cause toning when converted into ink-receptive material in actinic light.

As compared with the commercially available, water-developed negative-acting plates having a sensitized, superficially saponified cellulose acetate layer, as described, for instance, in Dutch patent application 6704183, this plate is advantageous because a clearly visible image is formed upon it after image-wise exposure and development with water. On the familiar plates no clearly visible image is formed, since the color of the completely exposed diazo resin contrasts hardly, if at all, with the color of the anti-halo layer that has to be present on the plate.

Sensitization of the negative-acting plate according to the invention is effected with an aqueous solution which contains, besides diazo resin, one or more acids for the stabilization of the light-sensitive layer.

The following examples illustrate practices of the invention:

EXAMPLE I

(A) A sheet of highly satinated paper of 125 g./m.² is coated with a water-repellent layer by the application of a liquid containing:

120 ml. of styrene-butadiene latex having a solids content of about 48%; the styrene-butadiene copolymer contains about 30% of styrene
70 ml. of an aqueous solution of a melamine formaldehyde resin (66.7%)

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200 g. of a 60% dispersion of clay in water
0.6 g. of ammonium chloride
7.2 ml. of ammonium hydroxide (technical)
12 ml. of isopropanol
50 ml. of distilled water.

The layer is dried. It weighs about 10 g./m.².

On the water-repellent layer an intermediate layer is coated by applying a liquid of the following composition:

50 ml. of styrene-butadiene latex of the above composition
55 ml. of a 20% aqueous solution of hydrolyzed starch
370 g. of a 60% dispersion of clay in water
17 ml. of an aqueous glyoxal solution (40%)
20 ml. of isopropanol.

The layer is dried. The dry layer weighs about 10 g./m.².

On the intermediate layer a planographic layer having a dry weight of about 10 g./m.² is formed by applying a dispersion of the following composition:

160 ml. of an aqueous solution of polyvinyl alcohol having a degree of hydrolysis of 99.8%, which contains
66 g. of polyvinyl alcohol per liter of water
142 g. of a 56.5% dispersion of titanium dioxide in water
32 ml. of an aqueous glyoxal solution (40%)
40 ml. of isopropanol
30 ml. of distilled water.

The layer is dried.

The planographic layer of the planographic printing plate thus obtained is sensitized with a liquid containing:

30 g. of 4-benzoylamino 2,5-dibutoxy benzene diazonium chloride zinc chloride double salt
10 g. of boric acid
2 g. of tartaric acid
1 ml. of wetting agent
400 ml. of isopropanol
580 ml. of distilled water

and dried.

The light-sensitive, positive-acting planographic printing plate thus obtained is exposed under a positive original having screen half-tones until underneath the white areas of the original all the diazo compound has bleached out, and is then developed with a liquid of the following composition:

12 g. of phloroglucinol
11 g. of citric acid
87 g. of disodium phosphate 2 aq.
1 g. of the potassium salt of hydroquinone monosulphonic acid
5 g. of thiourea
0.5 ml. of wetting agent
water up to 1 liter.

The pH of this developing liquid is about 7.

The developed plate is rinsed with water and placed on the offset printing press. 1500 prints of excellent quality were made.

(B) A second plate produced in the above manner is sensitized with a solution containing:

4 g. of zinc chloride double salt of a condensation product of p-diazodiphenylamine and formaldehyde, prepared in concentrated sulphuric acid
15 ml. of phosphoric acid (50%)
12 ml. of isopropanol
80 ml. of water

and dried.

The negative-acting plate thus obtained is exposed under a negative original having fine screen areas, after which the unexposed diazo resin is washed away with water. More than 1500 prints of excellent quality were produced from the planographic printing form thus obtained.

EXAMPLE II

(A) On the water-repellent layer applied according to Example I on a sheet of highly satinated paper of 125 g./m.² an intermediate layer having a dry weight of 10 g./m.² is formed by the application of a liquid as described in Example I, but which now contains 55 ml. of a 20% aqueous dextrin solution instead of 55 ml. of a 20% aqueous solution of hydrolyzed starch. The intermediate layer is coated with a planographic layer having a dry weight of 12 g./m.², by applying a coating liquid of the following composition:

90 ml. of an aqueous solution of polyvinyl alcohol having a degree of hydrolysis of 99.8%, containing 66 g. of polyvinyl alcohol per liter of water
70 g. of a 47% aqueous dispersion of titanium dioxide
10 ml. of an aqueous glyoxal solution (40%)
10 ml. of isopropanol
10 ml. of distilled water.

The layer is dried.

The planographic layer is sensitized with the sensitizing liquid for the positive-acting plate described in Example I. The positive-acting planographic printing plate thus obtained is converted into a planographic printing form by the method described in Example I. More than 1500 prints of very good quality were obtained from the printing form.

(B) The layer of planographic second plate produced in the above way is sensitized with a solution of the following composition:

6 g. of sulphate of a condensation product of p-diazodiphenylamine with formaldehyde prepared in concentrated sulphuric acid
17 ml. of phosphoric acid (50%)
20 ml. of isopropanol
120 ml. of water

and dried.

The negative-acting planographic printing plate thus obtained is converted into a printing form as described in Example I. 1600 prints of good quality were obtained from this printing form.

EXAMPLE III

(A) On a sheet of highly satinated paper of 125 g./m.² a water-repellent layer having a dry weight of 12 g./m.² is formed by applying the liquid described in Example I.

On the water-repellent layer an intermediate layer is formed by applying a liquid having the following composition:

50 ml. of styrene-butadiene latex having a solids content of 48%; the styrene-butadiene copolymer contains about 30% of styrene
100 ml. of an aqueous sodium alginate solution (7%)
340 g. of an aqueous dispersion containing 320 g. of colloidal silica and 560 g. of clay per liter of water
17 ml. of an aqueous glyoxal solution (40%)
20 ml. of isopropanol.

The layer is dried. The dry intermediate layer weighs about 10 g./m.². On this intermediate layer a planographic layer is applied as described in Example I.

The planographic layer is sensitized with the sensitizing liquid for the positive-acting plate described in Example I and dried.

The positive-acting planographic printing plate thus obtained is imagewise exposed and developed as described in Example I.

1500 good prints were produced from the planographic printing form thus obtained.

(B) A second plate is sensitized with the sensitizing liquid for the negative-acting plate described in Example I. The negative-acting plate thus obtained is converted into

a planographic printing form as described in Example I. More than 1500 good prints were obtained from this planographic printing form.

(C) Instead of 100 ml. of an aqueous 7% sodium alginate solution it is possible to use 100 ml. of an aqueous 7% hydroxy-ethyl cellulose or sodium carboxymethyl cellulose solution in the composition of the coating for the intermediate layer. The 50 ml. of styrene-butadiene latex can be replaced by 50 ml. of 46% polyethyl acrylate latex, or 50 ml. of 50% polymethyl methacrylate latex.

EXAMPLE IV

(A) A sheet of highly satinated paper of 125 g./m.² is coated with a water-repellent layer by applying a liquid of the following composition:

70 ml. of an aqueous solution (66.7%) of a melamine-formaldehyde resin
0.6 g. of ammonium chloride
7 ml. of ammonia (technical)
70 ml. of isopropanol
70 ml. of distilled water.

The layer is dried. On the water-repellent layer an intermediate layer having a dry weight of about 15 g./m.² is formed by applying a liquid containing:

50 ml. of 46% polyethyl acrylate latex
55 ml. of an aqueous 20% polyvinyl pyrrolidone solution
310 g. of a 71% dispersion of clay in water
17 ml. of an aqueous glyoxal solution (40%)
20 ml. of isopropanol.

The layer is dried. The intermediate layer is coated with a planographic layer having a dry weight of about 12 g./m.² by applying a liquid containing:

175 ml. of an aqueous solution of polyvinyl alcohol having a degree of hydrolysis of 99.8%, containing 66 g. of polyvinyl alcohol per liter of water
70 g. of a 57% dispersion of titanium dioxide in water
17 ml. of an aqueous glyoxal solution (40%)
35 ml. of isopropanol
20 ml. of distilled water
0.2 ml. of wetting agent.

The layer is dried. The planographic layer is sensitized with the sensitizing liquid for the positive-acting plate described in Example I, but which now contains 30 g. of 4-(4'-methoxyphenyl)thio - 5 - methoxy - 2 - N - methyl-N - ethoxycarbonylamino benzene diazonium chloride, zinc chloride double salt, instead of 30 g. of 4-benzoylamino - 2,5 - dibutoxy benzene diazonium chloride, zinc chloride double salt. The positive-acting planographic printing plate thus obtained is converted into a planographic printing form ready for printing as described in Example I. More than 1000 good prints were obtained from this planographic printing form.

(B) A second plate produced by the above method is sensitized with the sensitizing liquid for the negative-acting plate described in Example II and dried. The plate is converted into a planographic printing form as described in Example I. 1500 prints of good quality were obtained from this planographic printing form.

EXAMPLE V

(A) On a sheet of highly satinated paper of 125 g./m.² a water-repellent layer of about 10 g./m.² is formed by applying a liquid having the following composition:

50 ml. of 44% latex of a terpolymer containing 63% of ethyl acrylate, 35% of methacrylonitrile, and 2% of methacrylic acid
40 ml. of an aqueous solution of a polyvinyl alcohol having a degree of hydrolysis of 87-89%, containing 200 g. of polyvinyl alcohol per liter of water

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315 g. of an aqueous dispersion containing 1155 g. of clay and 1155 g. of barium sulphate per liter of water 17 ml. of an aqueous glyoxal solution (40%) 20 ml. of isopropanol.

The layer is dried. On this intermediate layer a planographic layer having a dry weight of about 12 g./m.² is formed by applying a liquid of the composition described in Example I, which contains in addition 3 ml. of water glass.

The planographic layer is dried and sensitized with the sensitizing liquid for the positive-acting plate described in Example I and subsequently dried. The light-sensitive planographic printing plate thus obtained is exposed and developed as described in Example I. The planographic printing form was placed in an offset printing press and more than 1500 prints of good quality were obtained from it.

(B) A second plate is sensitized with the sensitizing liquid for the negative-acting plate described in Example I. The negative-acting plate thus obtained is converted into a printing form as described in Example I. 1700 prints of good quality were obtained from this printing form.

While numerous details, examples and explanations have been set forth hereinabove to illustrate the practice and principles of the invention, it will be understood that the invention can be applied in various other ways and by the use of compounds and materials other than those particularly named. It is not intended to be restricted to particulars of the foregoing description except as may be required for fair construction of the appended claims.

What is claimed is:

1. A light-sensitive planographic printing plate comprising a paper support having coated upon a side thereof a water-repellent layer on the paper surface, an intermediate layer adhering to said water-repellent layer, and a planographic layer in adherence to said intermediate layer, the outer surface of said planographic layer having a light-sensitive coating thereon, wherein said intermediate layer consists essentially of finely divided filler dispersed in a binder mixture comprising a major proportion of hydrophobic thermoplastic film-forming polymer and a minor proportion of hydrophilic organic binder, said planographic layer consists essentially of finely divided filler dispersed in substantially water-insoluble cross-linked polyvinyl alcohol having a degree of hydrolysis of at least 98%, and said light-sensitive coating comprises a light-sensitive diazo compound that will form a water-insoluble ink-receptive image by an imagewise exposure of said light-sensitive coating to actinic light, said compound being a condensation product of a diazonium salt of a p-phenylene diamine and formaldehyde, or said compound comprises a benzene diazonium salt that has a higher coupling activity in aqueous solution than 1-diazo-4-N-methyl-N-cyclohexylamine-3-chlorobenzene and that will form an ink receptive azo dyestuff by coupling with phloroglucinol when said coating after imagewise exposure is developed with an aqueous buffered phloroglucinol solution having a pH of about 6-7.

2. A plate according to claim 1, the filler in said planographic layer being principally titanium dioxide.

3. A plate according to claim 1, said hydrophobic polymer having a softening temperature below 110° C.

4. A plate according to claim 1, said hydrophobic polymer being a polyacrylic or polymethacrylic ester or a copolymer of butadiene with styrene.

5. A plate according to claim 1, said hydrophilic binder being a starch derivative selected from the group consisting of hydrolyzed starch, oxidized starch, dextrin, hydroxyethyl starch, starch acetate and enzyme converted starch.

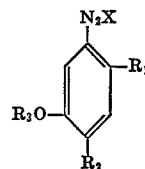
6. A plate according to claim 1, said hydrophilic binder being polyvinyl pyrrolidone.

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7. A plate according to claim 1, the filler in said intermediate layer being principally a finely divided clay.

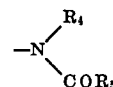
8. A plate according to claim 1, said intermediate layer containing 3-7 parts by weight of filler per part of said binder mixture and said binder mixture containing 0.3-0.7 part by weight of said hydrophilic binder per part of said film-forming polymer.

9. A plate according to claim 1, said diazo compound being a benzene diazonium salt having the formula:



in which X is an anion,

R₁ is an alkoxy group or a



group in which R₄ is alkyl, cycloalkyl or aralkyl and

COR₅ is an acyl group,

R₂ is an acylamino or a thioether group, and

R₃ is an alkyl group.

10. A plate according to claim 1, said film-forming polymer comprising a copolymer of styrene and butadiene.

11. A plate according to claim 1, said diazo compound being a 4-benzoylamino-2,5-dialkoxy benzene diazonium salt, whereby a positive water-insoluble ink-receptive image is formed by said exposure and said reaction.

12. A plate according to claim 1, said diazo compound being a condensation product of p-diazodiphenylamine and formaldehyde, whereby a negative water-insoluble ink-receptive image is formed by said exposure.

13. A plate according to claim 1, said diazo compound being a 4(4'-methoxyphenyl)thio-5-methoxy-2-methyl, ethoxycarbonyl amino benzene diazonium salt, whereby a positive water-insoluble ink-receptive image is formed by said exposure and said reaction.

14. A light-sensitive planographic printing plate comprising a paper support, a water-repellent coating on the surface of said support, on said coating a clay-filled water-insoluble coating of a mixture of a starch derivative and a copolymer of styrene and butadiene, containing 0.3 to 0.7 part by weight of the starch derivative per part of said copolymer and 3 to 7 parts by weight of finely divided clay per part of said mixture, said starch derivative being selected from the group consisting of hydrolyzed starch, oxidized starch, dextrin, hydroxyethyl starch, starch acetate and enzyme converted starch, on said clay-filled coating a TiO₂-filled coating of water-insoluble cross-linked polyvinyl alcohol having a degree of hydrolysis of at least 98%, and on the surface of the last-recited coating a light-sensitive coating consisting principally of a 4-benzoylamino-2,5-dialkoxy benzene diazonium salt.

15. A planographic printing plate comprising a paper support, a water repellent coating on the surface of said support, on said coating a clay-filled, water-insoluble coating of a mixture of a starch derivative and a copolymer of styrene and butadiene, containing 0.3 to 0.7 part by weight of the starch derivative per part of said copolymer and 3 to 7 parts by weight of finely divided clay per part of said mixture, said starch derivative being selected from the group consisting of hydrolyzed starch, oxidized starch, dextrin, hydroxyethyl starch, starch acetate and enzyme converted starch, and on said clay-filled coating a TiO₂-filled coating of water-insoluble cross-linked polyvinyl alcohol having a degree of hydrolysis of at least 98%, and on the surface of the last recited coating, a light-sensitive coating which comprises a light-

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sensitive diazo compound that will form a water-insoluble ink-receptive image by an imagewise exposure of said light-sensitive coating to actinic light, said compound being a condensation product of a diazonium salt of a p-phenylene diamine and formaldehyde, or said compound comprises a benzene diazonium salt that has a higher coupling activity in aqueous solution than 1-diazo-4-N-methyl-N-cyclo hexylamine-3-chlorobenzene and that will form an ink receptive azo dyestuff by coupling with phloroglucinol when said coating after imagewise exposure is developed with an aqueous buffered phloroglucinol solution having a pH of about 6-7.

16. A plate according to claim 15, and on the surface of the last recited coating a light-sensitive coating consisting principally of a condensation product of a 4-diazo-diphenylamine and formaldehyde.

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CHARLES L. BOWERS, Jr., Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,756,823

Dated September 4, 1973

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

Column 9, lines 54-55, and column 11, lines 5-6,
delete "said compound" and in place thereof
read:
--said light-sensitive coating--.

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents