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PLANOGRAPHIC PRINTING PLATE AND TREATMENT THEREOF

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This invention relates to paper plates, especially coated paper plates for planographic printing and to the preparation and treatment thereof.

Planographic or lithographic printing depends upon the immiscibility of water or aqueous wet-out solution and greasy lithographic printing ink. To print by lithography there is affixed to a suitable flat surface or plate an ink-receptive, water-repellent image, usually greasy, waxy, or resinous in nature. To the plate so imaged is then applied wet-out solution, usually an aqueous solution of glycerine or similar substance rendered slightly acidic as by addition of a phosphate or equivalent acidifying material. The wet-out solution wets all portions of the plate not already covered by imaging material, but it does not wet the water-repellent image. An inking roll coated with lithographic printing ink now passed over the plate leaves a film of ink upon the imaged areas but leaves no ink on the unimaged areas which already carry a film of the ink-repellent wet-out solution. The inked plate when brought into contact with an ink-receptive surface transfers thereto the ink in a pattern reverse to that on the plate. The surface so printed upon may be a paper sheet, but in most cases is an offset blanket which in turn transfers the print in form identical with that on the plate to a paper sheet which is the final printed matter. The plate is repeatedly dampened, inked and printed from until the desired number of prints have been made.

In recent years very substantial improvements have been made in the production of paper-base printing plates for lithographic or planographic printing. In general terms, such plates may be said to comprise a paper base, with or without wet-strength properties, and usually on at least one side of said base a layer of coating comprising hydrophilic film-forming material containing dispersed therein some filling material, usually inert, such as clay, blanc fixe, or the like. In some cases a light-weight wash coating of substantially clear hydrophilic film-former, i. e. free from filling material, is applied over the before mentioned filled coating in order to prevent excessive penetration by wet-out liquid, i. e., to afford improved hold-up of water, wet-out liquid or dampening solution. Another useful method of preventing such penetration, disclosed by S. V. Worthen in Patent No. 2,534,650, is by treating the surface with a soluble bivalent metal salt which by reaction with subsequently applied wet-out solution effectively prevents penetration of the latter through the coating.

Obviously it is essential that the image shall stick to the plate tenaciously. At the same time, the unimaged areas must be very easily and completely wet by water or aqueous wet-out or dampening solution and the latter should adhere tenaciously. Ideally the unimaged surface should be such that while it tenaciously holds water applied thereto it will permit no penetration of water. It has been usually found, however, that as hydrophilic surfaces improve in ability to withstand penetration by water they also tend to become less and less adhesive to imaging material and may become useless as printing surfaces because images will not stay fixed thereon.

The present invention provides a treatment of lithographic printing surfaces on plates formed of paper which substantially improves the ability of said printing surfaces when wet to withstand or resist being soiled by greasy ink, while at the same time it also improves the ability of the plates to retain lithographic images applied to the dry surface thereof.

In practice the invention comprises applying to a lithographic printing surface or plate comprising oxidizable organic matter an aqueous composition containing a dissolved compound of manganese of high valence (i. e., over 5 as for example in potassium permanganate) and reducing said manganese compound in situ to form a compound in which the manganese is in a lower state of valence (i e., under 5) than in the original compound. In some cases the compound of manganese having a valence below 5 is left distributed over the surface of the plate as a firmly adherent, water-insoluble, brownish residue the constitution of which is not known with certainty but which is presumed to be an oxide or hydroxide of manganese, e. g. manganese dioxide. In other cases, the aqueous composition besides the manganese compound also contains a soluble salt of a metal of valence greater than one, which is hereinafter referred to as a "multivalent metal"; and this is a preferred practice under this invention. In the latter case it appears that when the other multivalent metal present stands lower than manganese in the electromotive series, the reduced manganese seems to exist on the surface of the plate in the form of a water-soluble manganese salt and apparently an equivalent quantity of the other multivalent metal is left on the plate as an insoluble hydroxide or oxide. It is presumed that the maganese oxide or hydroxide formed by the reduction of the permanganate reacts with the multivalent metal salt to the formation of the corresponding manganese salt and the corresponding multivalent metal oxide or hydroxide. The multivalent metal salt may be used in quantity equivalent to or less than or more than equivalent to the reduced manganese compound.

When another multivalent metal salt is used in solution with permanganate it is obvious that the salt should not be one which is easily oxidized. Hence salts of organic acids are unsuitable for such use, as are also sulfites, nitrites, and the like. Such salts, however, can be applied to the plate surface either before or after the permanganate treatment. Soluble chlorides, nitrates and sulfates are suitable for use in the permanganate solution. Some of these salts, e. g. ferric chloride and to a lesser degree cupric chloride, are oxidized slowly by permanganate, but at the concentration used the reaction is so slow that it is of no consequence. That is, in a day's time, only an insignificant proportion of the permanganate will normally be reduced by such a salt. Cupric, ferric, zinc and chromic salts, particularly the chlorides, all give excellent results when used with permanganate as described. Apparently soluble salt of any metal can be used which will be precipitated as an insoluble hydroxide or oxide by the reduced manganese in the system. Some doubtless are more effective than others; naturally too those are preferred which are non-toxic or only slightly toxic, as well as those which are not unduly expensive.

The compound of high valent manganese applied may be any soluble salt of manganic or permanganic acid. The most readily available salt of this nature is potassium permanganate, but other available salts such as barium, sodium and zinc permanganates have given satisfactory results. In order that the manganese compound may be reduced there must be present some substance capable of being oxidized by said compound. In the case of paper-base lithographic plates there obviously will be sufficient organic matter at the surface of the plate to reduce the manganese compound. If the cellulose fiber making up the base is exposed to the action of the manganese compound it will itself act to reduce the latter; while in the case of a coated paper base the organic matter present in the coating will reduce the manganese compound. If desired, prior to the treatment by permanganate, a layer of reducing substance may be applied to the surface for the specific purpose of reducing the manganese compound; but such an application is not necessary in the case of paper base plates, nor ordinarily is it of any particular advantage.

There must of course be available sufficient reducing substance to react with all of the manganese compound originally applied. This requirement is not large, for only a small quantity of manganese compound need be applied, a light wash with a dilute solution (2%–10%) of potassium permanganate being the usual treatment.

When an insoluble manganese compound is formed by the reduction it adheres to or is bound by the organic reducing substance, or the oxidized product formed therefrom, so that the reduced insoluble manganese compound forms an integral part of the surface of the plate. One action of the so-deposited insoluble manganese compound is probably to plug to some extent the pores in the surface of the paper or coated paper treated. Another effect is a slight roughening of the entire surface which may provide a "tooth" for anchorage of imaging material and adherence of water or dampening solution in the unimaged areas of the plate surface.

As has been previously mentioned, when reduction of the high valent manganese compound takes place in the presence of a soluble salt of a multivalent metal standing below manganese in the electromotive series the reduced manganese will react with such multivalent metal salt to form a soluble manganese salt; and provided sufficient of such salt is present to react with all the reduced manganese, no insoluble manganese compound will be deposited. Instead there will be deposited an insoluble compound of said multivalent metal which to some extent at least exerts an action similar to that described above when an insoluble manganese compound is formed; namely, to provide a "plug" and "tooth." The soluble manganese salt doubtless in the manner described in the beforementioned Worthen Patent No. 2,534,650, reacts with subsequently applied wet-out solution to prevent undue penetration of such solution beneath the surface.

Besides the effects already mentioned, oxidizing action of the high valent manganese compound upon the organic matter serves to improve the hydrophilic properties of the surface so that it is more resistant to soiling by ink. In some cases at least, as in the case of starch coatings, the coating material also becomes more water-insoluble as a result of the oxidizing treatment, at the same time that it becomes less liable to toning by ink.

There seems likewise to be some further cooperating action between the permanganate and the soluble multivalent metal salt. For instance, it is fairly well-known that trivalent metal salts applied to the surface of a coated paper planographic printing plate tend with time to develop water-shedding or water-repellent qualities in that surface. When used with permanganate, however, the development of such water-repellency is to a large extent prevented or at least considerably slowed up, so that it is entirely feasible to use ferric salts or even aluminum salts together with permanganate to produce plates which have good storage properties.

I have found it to be advantageous also to apply a finely divided inorganic pigment in conjunction with the use of the permanganate and the soluble multivalent metal salt. This pigment should not be enveloped in and bonded to the paper by means of an adhesive as in the case of the pigment in paper coating compositions but should be applied to the surface of the paper in the form of an aqueous dispersion, free of adhesive. A preferred material for this purpose is a silica aquasol, i. e. an aqueous suspension of colloidal silica such as is described in U. S. Patent No. 2,375,738. It seems probable that the pigment especially the silica aquasol, also may contribute to the plugging of the pores and also to the provision of "tooth" on the surface of the plate to be helpful in holding the image as well as water on the surface thereof.

A planographic plate treated according to the invention is improved both for direct lithography and for photolithography. Paper base plates of quality so poor that they are entirely unsuitable for use may, when treated with permanganate solution, become quite satisfactory for use. Plates already of good quality may, when treated according to the invention, become considerably better so that they may then be rated as excellent or superlative in quality.

Example 1

A wet-strength paper web weighing 30 pounds per 1000 square feet was prepared from a furnish containing paper-making fibers, rosin size, melamine-formaldehyde reaction product, and aluminum sulfate. The formed web was then surface-sized with a solution of ammoniacal casein made slightly acidic by addition of commercial formaldehyde solution. The web, when dry, was coated on each side with 6 pounds dry weight per 1000 square feet of a mixture containing 100 parts clay, 20 parts casein, and 1½ parts dimethylolurea. The coated paper was dried and calendered. It was then washed on one side with a 5% aqueous solution of potassium permanganate, which when it had dried, left the treated surface quite brown in color. The so-treated surface was then used successfully for offset printing on an office type offset duplicator both when a direct image was affixed to the treated surface and also when an image was affixed photolithographically by the use of chromate sensitized albumin. The clay-and-casein coated paper before treatment with permanganate solution was not suited for use for planographic printing as it was soiled all over by lithographic ink almost immediately.

Example 2

A paper-base plate was prepared from a wet-strength base coated with a fairly thick layer of insolubilized sodium alginate. This surface was extremely resistant to soiling by ink when wet, but it was not sufficiently adhesive to a directly applied image to hold the image for more than a few impressions. The sheet was washed over with a 3% aqueous solution of potassium permanganate and dried. It was then found to hold a directly applied image well, and gave excellent results when used as an offset plate.

Example 3

Varnishable uncoated supercalendered paper is made according to the Cates U. S. Patent No. 2,088,893. Such paper is made from a furnish containing usual paper-making fibers, clay, rosin size, and alum, beaten until free from clumps of fibers. The furnish is formed into a web of close formation and the web is calendered heavily while the surface is wet. The resulting sheet has even formation, a high densometer value and a smooth surface. It ordinarily has no wet-strength properties. A sheet of this kind of varnishable uncoated one-side supercalendered paper having a basic weight of 55 pounds, 25" x 38"—500, was washed on the supercalendered side with a 6% solution of potassium permanganate in water, and dried. The so-treated sheet was typed upon by means of a typewriter and then was placed in an offset duplicator where it served as an offset planographic printing plate. Over 50 good copies were made therefrom before the plate, not being of wet-strength quality, became torn. The unimaged areas of the plate were still free from soil when the plate failed from tearing. It was not possible to obtain a single satisfactory print from the supercalendered paper before it had been treated with permanganate.

Example 4

A strong paper base was coated with an impregnating coating of urea-formaldehyde resin which left a layer of the resin over the surface. The coated paper was aged for several months and was distinctly water-repellent and not usable as a lithographic plate. The surface was swabbed with a 2½% aqueous solution of potassium permanganate and dried. It was then brown in color, and was readily wettable by water and by wet-out solution containing glycerine. An image was typed on the dry, treated surface and then the imaged surface was used as an offset plate with very satisfactory results.

Example 5

The process described in Example 1 was repeated with the substitution of a 3% sodium permanganate solution for the 5% potassium permanganate solution of said example. The results were similar to those reported in Example 1.

Example 6

The process described in Example 1 was repeated with the substitution of a 3% zinc permanganate solution for the 5% potassium permanganate solution of said example. The results were similar to those reported in Example 1.

Example 7

The coated paper sheet of Example 1 after it had been treated with potassium permanganate solution and dried was washed over with a sensitizing solution containing egg albumin 30 parts, ammonium dichromate 16 parts, diammonium phosphate 11 parts, and water 540 parts with a little ammonia to ensure alkalinity of the solution. The so-treated sheet was dried and exposed through a negative to actinic radiation. The exposed sheet was then washed to remove unexposed albumin coating and then used as a plate on an offset press where it gave satisfactory results.

Example 8

The same clay coated paper used in Example 1, after being dried and lightly calendered, was wash-coated with about 0.8 pound, dry weight, per thousand square feet of a 1% aqueous solution of the sodium salt of low viscosity carboxymethylcellulose. The sheet was dried and then washed with 15% phosphoric acid solution, rinsed and redried. At this point the sheet was fairly satisfactory for use as a planographic plate. When an image was typed on it with a typewriter, several hundred copies were printed from it before the background became too soiled for use. Part of the sheet before having an image affixed to it was washed with a 2% aqueous solution of potassium permanganate and dried. An image was typed on the permanganate treated surfaces as before, and the plate so made, before becoming soiled, gave over twice the number of good prints that the plate without permanganate treatment had given.

Example 9

The permanganate treated and dried sheet of Example 8 was coated with the sensitized albumin coating described under Example 7. The plate was dried and exposed through a negative to actinic radiation. The unexposed portions of the sensitized coating were removed by sponging, and the plate was then run on an offset duplicator where it gave satisfactory results.

Example 10

Paper weighing 50–60 pounds per ream (500 sheets, 25 by 38 inches) sized but not especially treated to give it wet-strength, was coated on one side with a starch-clay-dimethylolurea coating, about 6 pounds of coating (dry weight) per 1000 square feet of paper, dried and calendered. It was then coated on the already coated side with an aqueous composition containing 4 parts by weight of potassium permanganate, 8 parts by weight of

cupric chloride (anhydrous), 1.5 parts by weight of colloidal silica (dry basis), 86.5 parts by weight of water and then dried and supercalendered and was ready for use. The dry weight of the applied coating was about 1.8 pounds per ream (500 sheets, 25 by 38 inches).

Example 11

Paper similar to that described in Example 10 was coated, on the coated side with the following composition: 4 parts by weight of potassium permanganate, 4.8 parts by weight of ferric chloride (anhydrous), 3 parts by weight of colloidal silica, 88.2 parts by weight of water, and then dried and supercalendered and was ready for use. The dry weight of the coating was about 1.7 to 2 pounds per ream.

Cupric nitrate may be substituted for cupric chloride in Example 10 and ferric nitrate may be substituted for ferric chloride in Example 11 with similar results.

The concentrations of the solutions of permanganate and metal salts used in the foregoing examples may vary within a wide range. Generally the more concentrated are the applied solutions the better will be the results.

This application is a continuation-in-part of my abandoned application Serial No. 35,743, filed June 28, 1948.

I claim:

1. Process for improving a planographic printing surface on a paper base, said surface comprising a reducing organic material, which comprises uniformly wetting said surface with an aqueous solution of a water-soluble permanganate, said solution being substantially free of non-volatile organic film-forming material, and drying said surface.

2. Process as defined in claim 1 in which the surface is that of an organic hydrophilic colloid coating on the paper base.

3. Process as defined in claim 1 in which the surface is that of uncoated paper.

4. Process as defined in claim 1 in which the solution of permanganate contains also a water-soluble multivalent metal salt which does not reduce permanganate.

5. Process as defined in claim 1 in which a solution of a multivalent metal salt other than a salt of manganese is applied to the paper separately from the permanganate solution.

6. Process as defined in claim 1 in which the solution of permanganate contains a suspension of finely divided inorganic pigment.

7. Process as defined in claim 1 in which the solution of permanganate contains a water-soluble salt of a multivalent metal which does not reduce permanganate and which reacts with oxy compounds of manganese in which the manganese has a valence less than 5 to the formation of a water insoluble compound of said multivalent metal.

8. Process as defined in claim 4 in which the multivalent metal salt is a salt of a metal of the group consisting of iron, copper, zinc, chromium and aluminum.

9. Process as defined in claim 5 in which the multivalent metal salt is a salt of a metal of the group consisting of iron, copper, zinc, chromium and aluminum.

10. A planographic printing plate having a paper base and a preformed surface layer of a reducing organic material and uniformly distributed upon the surface only of said surface layer the reaction products of said organic material and a manganese compound in which the manganese has a valence greater than 5, said reaction products comprising a manganese compound in which the manganese has a valence of less than 5, said last named manganese compound having been formed on said surface from a solution of said manganese compound in which the manganese has a valence greater than 5 by the reducing action of the organic material in said surface layer upon the latter manganese compound.

11. A planographic printing plate as defined in claim 10 in which the surface layer consists essentially of an organic hydrophilic colloid.

12. A planographic printing plate as defined in claim 10

in which the printing surface is that of uncoated paper.

13. A planographic printing plate as defined in claim 10 in which the printing surface has distributed thereon a water insoluble compound of a multivalent metal other than manganese.

14. A planographic printing plate as defined in claim 10 in which the printing surface has distributed thereon a finely divided inorganic pigment.

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