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PAPER PLANOGRAPHIC PRINTING PLATE WITH STABILIZED HYDROPHILIC COATING

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This invention relates to coated paper base planographic printing plates and to methods of producing such plates.

Planographic printing is printing from plane surfaces, that is level surfaces without either raised or intaglio areas. Such printing depends upon the immiscibility of grease and water, or more specifically, of greasy lithographic printing-ink and aqueous lithographic solutions. To print by the planographic printing process or plane lithography there is affixed to a suitable printing surface or plate a water-repellent image usually greasy, resinous, or waxy in nature. To the plate so imaged is then applied aqueous wet-out liquid, such as a solution of glycerine slightly acidified with phosphoric acid, acid phosphates or similar substances. The aqueous wet-out liquid wets all portions of the plate surface not already covered by the water-repellent imaging material, but does not, of course, wet the water-repellent image. An inking-roll coated with lithographic printing ink now passed across the surface of the plate leaves a film of ink upon the ink-receptive imaged areas but leaves no ink on the unimaged areas which are already covered by a film of ink-repellent aqueous liquid. When the inked plate is brought into contact with another ink-receptive surface it transfers ink thereto in a pattern reverse to that on the plate. The surface so printed upon may be a paper sheet, but in most cases is a rubber offset blanket which in turn transfers the print in original form 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.

A requisite for a satisfactory plate is that when dry the plate shall readily accept a water-repellent image which must adhere tenaciously thereto and shall neither be pulled away by printing-ink nor be washed away by aqueous lithographic solutions. Another requisite is that all unimaged areas of the plate shall be readily wetted by aqueous lithographic solution and shall hold a film thereof on the surface of said unimaged areas and shall not permit the aqueous film to be displaced therefrom by printing ink.

The original material used for lithographic plates was a slab of limestone, but grained metal plates have been the commonly used material. Recently, however, coated paper planographic printing plates have come into extensive use, especially for small size plates in comparatively short runs as on office offset duplicators. It is with coated paper planographic printing plates that the present invention is concerned.

There are currently being made by several different manufacturers coated paper planographic printing plates of good quality. In general terms such a coated paper planographic printing plate may be said to comprise a paper base, which preferably but not necessarily possesses wet-strength properties, the paper base bearing on at least one surface a layer of coating comprising a water-insoluble hydrophilic film-forming adhesive material such as casein, carboxymethyl-cellulose, or polyvinyl alcohol, said hydrophilic film-forming material containing dispersed therein some finely divided mineral filler or pigment material such as clay, blanc fixe or titanium dioxide.

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In United States Patent No. 2,534,650, I have disclosed and described the inclusion in such coating layers containing mineral pigment and hydrophilic adhesive of effective quantities of water-soluble salts of bivalent metals. Among the benefits resulting from the presence of such soluble salts of bivalent metal is a marked improvement in the ability of the coating layer to resist penetraton by aqueous lthographic solutions and also the consequent better holdup of such aqueous lithographic solutions upon the coated surface in position to repel printing ink therefrom as intended. Moreover, the beneficial effects of such soluble bivalent metal salts in the planographic printing surfaces is enduring over a period of years and so may be said to be permanent for the normal life of a paper base planographic printing plate.

In decided contrast to the effect in a planographic printing surface of soluble salts of bivalent metals is the effect normally produced by soluble salts of metals having a valence greater than 2; i. e., salts of multivalent metals such as trivalent and tetravalent metals. Metals having a valence greater than 2 are designated as "multivalent metals" (see Hackh's Chemical Dictionary published by Blakiston in 1929). Many soluble salts of multivalent metals do exert a transient beneficial effect when incorporated in the surface of a coated paper planographic printing plate. The beneficial effects of such salts, however, normally last only from a few hours or days to a very few weeks, and thereafter the good effects cease and deleterious effects set in. That is, in a short time the so-treated surface begins to develop a tendency to repel or shed water. When that occurs the unimaged surface is no longer sufficiently wetted by aqueous lithographic solution and in consequence it picks up ink over the whole area and becomes useless as a printing plate.

There seems to be no generally agreed upon explanation as to why coated paper treated with such soluble salts of multivalent metals become

water-repellent. Apparently the originally soluble salt is, in part at least, converted, perhaps by hydrolysis to a water-insoluble and water-repellent compound or form. For example, when zirconium acetate is used to water-proof textiles it has been stated that the water-repellent effect results from hydrolytic formation of water-insoluble basic zirconyl acetate. Whatever the explanation may be it is a fact that coated paper treated with such multivalent metal salts gradually, and in a comparatively short time, does develop water-repellent qualities which make it unsuitable for use as a planographic printing plate. It is a purpose of the present invention to make possible the use of such multivalent metal salts with coated paper planographic printing plates (and at the same time) by substantially preventing or very greatly retarding development of water-repellent properties. I have found that by associating the multivalent metal salts with certain uni-univalent salts not only are the multivalent metal salts made available for use in place of the bivalent metal salts but in general plates treated with multivalent metal salt in association with uni-univalent salt have a longer image life and give prints of better quality than comparable plates treated with bilvalent metal salts.

In the preferred practice of the invention a paper base, preferably one having wet-strength or water-proof qualities, is provided with a coating comprising finely divided mineral filler or pigment and adhesive matter having hydrophilic properties. The coating so formed has interstices or pores in its surface, which interstices are filled at least partially with a water-soluble salt of a multivalent metal and an organic acid, e. g., formic acid or acetic acid, in association with a substantial quantity of an alkali metal or ammonium salt of an organic acid, e. g., formic acid or acetic acid which is capable of forming a water-soluble salt with the particular multivalent metal present in the multivalent metal salt used. The action of the organic salt of the alkali metal or ammonium is not fully understood but the effect of its presence is to prevent or very greatly retard the development of the water-repellent or water-shedding effects which otherwise would result from the multivalent metal salt present. The alkali metal or ammonium salt may be applied simultaneously with the multivalent metal salt or the two salts may be applied in separate steps. For example, a solution containing both the multivalent metal salt and the alkali metal salt may be applied to the coated paper or a solution of either salt may be applied and dried followed by application of a solution of the other. Or the alkali metal or ammonium salt may, if desired, be included in the pigment-adhesive coating composition at the time of its application, while the multivalent metal salt may be applied subsequently as an aqueous wash. In cases where the aqueous adhesive-pigment coating composition is one which is not coagulated by the multivalent metal salt, the said multivalent metal salt may be included in the coating composition together with the alkali metal or ammonium salt or the latter may be applied subsequently.

When either salt is included in the pigment-adhesive coating it generally is necessary to use a greater quantity of the salt per unit of paper area than when the salt is applied to the surface of the coating because only the salt present in and adjacent the surface of the coating is effective.

At present I believe that the beneficial effects resulting from inclusion of water-soluble multivalent metal salt in the pores of the hydrophilic coated surface of the coated paper planographic printing plates of the invention may be explained as follows. The solution of multivalent metal salt undoubtedly enters the pores and interstices existing among adjacent particles of mineral pigment in the coating, and after evaporation of the aqueous vehicle the dry but still soluble salt remains deposited in and partially fills the said pores and interstices. When the surface is subsequently treated with an aqueous lithographic wet-out or fountain-solution which contains an ingredient capable of reacting with said soluble multivalent metal salt to form a less soluble or insoluble compound, such an insoluble or slightly soluble compound of the multivalent metal is formed in situ in the pores and interstices of the coating. The insoluble or slightly soluble multivalent metal compound so formed acts to plug the said pores and interstices and to a considerable extent prevents or decreases further penetration of the surface by lithographic solutions. Consequently, when lithographic fountain-solution is applied to the planographic printing plate having such a plugged surface, the solution remains substantially entirely upon the coated surface of the plate where it is effective in accomplishing its intended purpose of preventing contact between the said surface and the printing-ink on the inking-rollers of the lithographic printing press upon which the plate may be used.

It is apparent that for the multivalent metal salt to accomplish the desired results it must exist in the pores in soluble condition up to the time the plate is prepared for use on the printing press. That means that the salt must be used in quantity in excess of the amount which will be consumed by possible reaction with the adhesive or other components of the coating with which it is used and that it must not be transformed by hydrolysis into an insoluble compound of the metal.

The results accomplished by use of multivalent metal salts of organic acids together with alkali metal or ammonium salts according to the invention closely resemble those produced by use of bivalent metal salts according to the beforementioned Patent No. 2,534,650. In said Patent No. 2,534,650, I pointed out the general unsuitability of soluble salts of multivalent metals alone for use in coated paper planographic printing plates owing to the lack of stability of such multivalent metal salts upon aging of plates containing them. The excellent results obtained by use of multivalent metal salts in conjunction with alkali metal or ammonium salts according to the present invention are due in part to the discovery that the presence of alkali metal or ammonium salts of the lower aliphatic acids, i. e., formic and acetic acids, are effective to promote stability of multivalent metal salts upon ageing so that the original beneficial qualities of such multivalent metal salts may be extended over prolonged periods of storage of coated paper planographic printing plates in which they may be used.

The treatments of the present invention may be applied to any of the types of coated papers which are suitable for treatment by bivalent metal salt solutions according to the aforementioned Patent No. 2,534,650. The treatment is particularly efficacious in preparation of coated paper planographic printing plates for printing comparatively long runs of upwards of ten thousand copies to as much as thirty thousand copies. The following Example 1 is an embodiment of the invention suitable for printing such long runs.

EXAMPLE 1

Step 1.—A wet-strength paper web of approximately 95 pounds weight, based on a ream of 500 sheets cut to a size of 25 x 38 inches, may be prepared from a paper-making furnish containing beaten fibers from deciduous trees and from coniferous trees in approximately equal quantities, rosin-size, melamine-formaldehyde resin, and alum. The fiber from deciduous trees may be replaced in whole or in part by fiber from coniferous trees, and clay or other suitable filler, although not particularly desirable, may be included in the furnish. The formed web is then preferably but not necessarily surface-sized with an aqueous solution of ammoniacal casein made slightly acidic with formaldehyde. Between one and two pounds (dry weight) of the casein size, per ream, should be taken up. The web may then be dried and machine-calendered.

In place of the materials employed to impart wet-strength to the paper base sheet made in accordance with the foregoing Step 1, namely, the melamine-formaldehyde resin and the ammoniacal casein-formaldehyde wash surface-size, other known materials may be employed for imparting wet-strength to the paper base sheet and among these are urea-formaldehyde resin, glue-formaldehyde, viscose, and other materials. The use of the casein-formaldehyde wash, referred to in the foregoing Step 1, alone will provide a usable paper base sheet having fairly good wet-strength, but I prefer to use both it and the melamine-formaldehyde resin.

Step 2.—A paper base sheet web prepared in the manner set forth in the foregoing Step 1 may be coated on one side, which will be the reverse or non-printing side of the finished paper plate, with about 10 pounds, dry weight, per ream of a composition containing 100 parts of clay, 18 parts of casein, and 1¾ parts of dimethylol urea, and the sheet is again dried. The function of this coat is merely to promote flatness of the finished product by counteracting the tendency to curl caused by subsequent application of coating to the other, or printing side, of the sheet.

Step 3.—To the previously uncoated side of the paper web may be applied about 10 pounds dry weight, per ream, of a barrier coat deposited from an aqueous composition containing dry weights according to the following Formula 1.

Formula 1:	Parts by weight
Pigment (finely divided clay)	50
Copolymer of 60 styrene-40 butadiene (in primary emulsion)	60
Polystyrene, high molecular weight (in primary emulsion)	40

The coating is then well dried.

The term "primary emulsion" as used in preceding Formula 1 is used to designate an aqueous emulsion in which the polymeric substance therein has been polymerized in situ. The purpose of the barrier coat of Formula 1 is to prevent saturation of the paper fibers by fountain-solution during long runs; any barrier coat may be used which will accomplish this purpose and which is sufficiently non-tacky so that the coated paper may be rolled up without sticking together and which is satisfactorily wettable by the aqueous coating composition of hydrophilic material to be subsequently applied thereto. Other film-formers which have been found useful for barrier coats include urea-formaldehyde resin, butadiene-acrylonitrile copolymer, polymerized methyl acrylate, plasticized polyvinyl chloride, plasticized polyvinyl butyral, and the like. The inclusion of mineral filler or pigment in the barrier coat is optional; the filler acts to decrease tackiness and also probably serves as an anchor for the coating subsequently applied thereto.

Step 4.—A coated paper web as prepared in the manner set forth in the foregoing Step 3 may be coated on top of the barrier coat of Step 3, with from 8 to 14 pounds, with an optimum of 12 pounds per ream, dry weight, of a mixture having the composition set forth in the following Formula 2 so as to provide a pigmented hydrophilic coating containing interstices which provide capillary spaces or pores:

Formula 2	Parts by weight
Pigment (finely divided clay)	100.0
Hydrophilic adhesive (casein in water solution of ammonia)	18.0
Dimethylol urea (to insolubilize the casein)	1.75

The paper base sheet or web bearing the pigmented hydrophilic adhesive coat of the foregoing Formula 2 thereon may then be suitably dried as, for example, at a temperature of from 120° F. to 140° F. for a period of from 10 to 20 minutes, and calendered, although calendering is not essential.

Step 5.—The thus coated and calendered paper base sheet may then be washed, on the side having the pigmented hydrophilic adhesive coat of Step 4, with an aqueous solution containing an acetate or formate of a multivalent metal and a stabilizer comprising an alkali metal or ammonium formate or acetate similar to that of the following formula:

Formula 3	Parts by weight
Zirconium acetate (zirconyl acetate)	15
Sodium acetate	5
Butanol	2
40% formaldehyde solution	1
Water	77

The sheet is then again dried.

Step 6.—The dried coated and treated sheet may then be rubbed against rotating brushes. While not essential to or indispensable in the practice of the present invention, this operation of rubbing or brushing the face of the printing surface of the new paper base planographic printing plates increases the image-reproducing life of the plates and improves the quality of the images reproduced from the treated plates. Moreover, this operation of rubbing or brushing the face of the plate tends to remove any excess of the multivalent metal salt, or of the alkali metal or ammonium salt, which may crystallize on the surface of the plate.

The improvement in paper base planographic printing plates which resides in rubbing or brushing the printing surface of such plates forms the subject matter of Patent No. 2,534,588 and hence no claim is made herein to said improvement except insofar as the same may be employed as a final step in the process of making coated paper base planographic printing plates according to the present invention.

The butanol employed in Formula 3 of Step 5 preceding, while not essential in the practice of the invention, facilitates and promotes penetration of the water-soluble salt solution into the capillary spaces formed by the pores or interstices among the finely divided mineral particles in the coating. In place of butanol, equivalent volatile water-miscible solvents including meth-

anol, ethanol, propanol and the like may be used.

The formaldehyde included in Formula 3 of Step 5 preceding is not essential in practice of the invention, and is used to hasten the attainment of water-insolubility of the casein in the pigmented hydrophilic coating which otherwise might take somewhat longer to develop.

The clay-casein ratio in the clay-casein hydrophilic coating of foregoing Formula 2 may be varied widely from about 12 to 75 parts of casein per 100 parts of clay, and the weight of the clay-casein coating may be varied from 6 to 30 pounds per ream of paper.

In place of the clay-casein hydrophilic coating referred to in Formula 2 for use in practicing the present invention, other suitable pigmented hydrophilic adhesive coatings which may be employed include those containing the following hydrophilic adhesive base materials: glue, gelatine, soy bean protein, zein, insolubilized starch, polyvinyl alcohol, carboxymethyl cellulose, hydroxyethyl cellulose, gum arabic or any other equivalent hydrophilic adhesive base material which may be pigmented and rendered water-insoluble while still remaining hydrophilic.

Moreover, the clay or pigment component of the pigmented hydrophilic adhesive or clay-casein referred to in foregoing Formula 1 may be replaced in whole or in part by other suitable finely divided mineral pigments including barium sulfate, calcined clay, talc, titanium dioxide and other equivalent finely divided mineral pigments.

In place of the zirconium acetate of Formula 3 of Step 5 preceding there may be used other soluble acetates or formates of multivalent metals. In general these multivalent metal salts may be used in solutions ranging from about 4 percent concentration to about 25 percent concentration or to the limit of the solubility range in cases where it is lower than about 25 percent.

In place of the sodium acetate used in Formula 3 of Step 5 to stabilize the multivalent metal salts, there may be used in aqueous solution the acetate or formate of ammonium or of any alkali metal. Useful concentrations of such ammonium or alkali metal salts range from about 1 percent to a concentration equal to the concentration of the multivalent metal salt present. No advantage exists in using an amount of stabilizing salt greater than the amount of the multivalent metal salt present. Generally it is adequate to use a quantity of stabilizing salt equal to from one-fifth to one-half of the weight of multivalent metal salt present.

The following table shows various examples of combinations of multivalent metal salt and ammonium or alkali metal salt which have satisfactorily replaced the 15 percent of zirconium acetate and 5 percent of sodium acetate in Formula 3 of Step 5.

Table

	Percent by weight
Aluminum acetate	15
and Sodium acetate	5
Aluminum acetate	15
and Sodium formate	5
Aluminum formate	15
and Sodium formate	5
Aluminum formate	15
and Sodium acetate	5
Chromic acetate	9
and Sodium acetate	5
Ferric acetate	10
and Sodium acetate	5
Uranium acetate (uranyl acetate)	12
and Sodium acetate	5
Zirconium acetate (zirconyl acetate)	15
and Sodium acetate	1
Zirconium acetate	5
and Sodium acetate	5
Zirconium acetate	25
and Sodium acetate	10
Zirconium acetate	15
and Sodium formate	5
Zirconium acetate	15
and Potassium acetate	5
Zirconium acetate	15
and Lithium acetate	5
Zirconium acetate	15
and Ammonium acetate	5

Every one of the multivalent metal salts listed in foregoing table when applied alone to a hydrophilic coated surface, i. e., when used without having a stabilizing ammonium or alkali-metal formate or acetate present, soon develops water-shedding qualities in the surface which thereby becomes unfit for use as a planographic printing plate. On the other hand, when the multivalent metal salt is used in conjunction with a stabilizing ammonium or alkali metal salt as shown in the table, a very marked increase in useful life of the plate results in every case. In some cases most pronounced effects are produced by use of the ammonium or alkali metal salt followed by rubbing according to the before-mentioned Patent No. 2,534,588.

In applying the solution of mixed multivalent metal salt and alkali metal salt of Formula 3, or any of the other mixtures of multivalent metal salts and alkali metal or ammonium salt of the table, or mixture thereof, the amount of salt solution applied is preferably maintained within a range of from one-half gallon to five gallons per ream. The optimum quantity in any particular case will naturally depend in part upon the specific salts used as well as upon the degree of absorbency of the coated surface to which the solution is applied. In most cases, use of from one to two gallons per ream produces very satisfactory results. In a specific case of a coated base which was identical with the one described in Example 1, a salt solution corresponding to that of Formula 3, and which had a specific gravity of 1.125, was used at the rate of 1.25 gallons per ream of paper treated.

EXAMPLE 2

A medium run plate capable of printing up to 1000 copies was made by following the procedure of Example 1 with the following exceptions:

In Step 1, a wet-strength paper web of approximately 75 pounds weight per ream was used instead of the heavier base used for the long run plate, and the barrier coat of Step 3 was entirely omitted.

EXAMPLE 3

A short-run plate capable of printing up to 300 copies was made in a manner similar to that of Example 2, except that a 60 pound paper base was used, and the wet strength treatment of Step 1 was entirely omitted.

The coated paper base planographic printing plate of the invention, previously described, may have the printing image affixed thereto, by any direct process, such as by a printing press or typewriter, by greasy pencil or crayon, by a pen using

oily writing fluid such as is commonly used in the so-called "ball-point" pens, or the like. Or, if desired, the plate may be photo-sensitized by application thereto of bichromated albumin or similar sensitizer, and a photo-image may be affixed thereon, by exposure of the sensitized surface to actinic radiation through a negative or other mask having both transparent and opaque areas. Such photo-sensitization of the plate is described in the following Example 4.

EXAMPLE 4

A coated paper planographic printing plate identical with one made according to Example 1, preceding, was sponged over with the composition of the following Formula 4.

Formula 4:	Parts by volume
Albumin in aqueous solution of 8° Baumé	30
Ammonium bichromate in 20% aqueous solution	18
Water	100

The sheet so sensitized was dried in the absence of light and was then exposed through a half-tone negative to radiation from a carbon-arc for about 3 minutes. The exposed surface then was swabbed with a sponge, wet with water, followed by an application of a commercial lithographic wet-out solution; then the plate was used on a rotary offset duplicator to produce several hundred satisfactory copies.

It will be seen from the foregoing description that the invention provides new and improved coated paper base planographic printing plates having the advantages and desirable characteristics mentioned, and others which are inherent in coated paper base planographic printing plates prepared in accordance with the invention.

It will also be seen that the invention provides new and improved compositions and processes for preparing the new coated paper base planographic printing plates.

I claim:

1. A planographic printing plate comprising a paper base having thereon a planographic printing surface layer, said layer comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment and having therein capillary interstices and pores containing the evaporation residue of an aqueous solution containing a water-soluble multivalent metal salt of an acid of the group consisting of formic acid and acetic acid in quantity in substantial excess of that required for reaction with other ingredients of said layer and the evaporation residue of an aqueous solution containing a water-soluble uni-univalent salt of the group consisting of the alkali metal and ammonium salts of the acids of the group consisting of formic acid and acetic acid in quantity amounting to at least one-fifth of the weight of the multivalent metal salt.

2. A planographic printing plate as defined in claim 1 in which the multivalent metal is a member of the group consisting of aluminum, chromium, iron, uranium and zirconium.

3. A planographic printing plate as defined in claim 1 in which the multivalent metal is zirconium.

4. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is zirconium acetate.

5. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is zirconium formate.

6. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is an acetate.

7. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is a formate.

8. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is an acetate and the uni-univalent salt is an acetate.

9. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is an acetate and the uni-univalent salt is a formate.

10. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is a formate and the uni-univalent salt is an acetate.

11. A planographic printing plate as defined in claim 1 in which the multivalent metal salt is a formate and the uni-univalent salt is a formate.

12. Process for the production of a planographic printing plate which comprises coating a paper base sheet with an aqueous coating composition comprising hydrophilic adhesive material and a finely divided mineral pigment resulting, when dried, in a surface having therein capillary interstices and pores, and incorporating into said surface the evaporation residue of an aqueous solution containing a water-soluble multivalent metal salt of an acid of the group consisting of formic acid and acetic acid in quantity in substantial excess of that required for reaction with the coating and the evaporation residue of an aqueous solution of a uni-univalent salt of the group consisting of the alkali metal and ammonium salts of an acid of the group consisting of formic acid and acetic acid in quantity amounting to at least one-fifth of the weight of the multivalent metal salt.

13. Process as defined in claim 12 in which a single aqueous solution containing both the multivalent metal salt and the uni-univalent salt is applied to the dried coating of hydrophilic adhesive material and mineral pigment.

14. Process as defined in claim 12 in which separate aqueous solutions of the multivalent metal salt and the uni-univalent salt are successively applied to the dried coating of hydrophilic adhesive material and mineral pigment.

15. Process as defined in claim 12 in which both the multivalent metal salt and the uni-univalent salt are incorporated into an aqueous coating composition which is not coagulated thereby.

16. Process as defined in claim 12 in which the uni-univalent salt is incorporated into the aqueous coating composition and the aqueous solution of the multivalent metal salt is applied to the dried coating.

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