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PLANOGRAPHIC PRINTING PLATE AND METHOD OF MAKING SAME

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1

This invention relates to coated paper base planographic printing plates and to a method of making such plates.

Paper base planographic printing plates are used in place of lithographic stones or metal plates commonly employed in lithographic printing. In the use of such planographic printing plates, as in the use of lithographic stones and metal plates, the matter to be reproduced (i. e. the image), whether a drawing, writing or printing, is inscribed on the surface by the use of some substance, usually greasy, for instance by a crayon, pen and ink, or a writing machine. If water is then applied to the surface of such a plate, those areas comprising the image will resist wetting by water due to their greasy surface, and then, when ink is applied to the plate, the ink will transfer only to the areas composing the image and not to the areas which have been wet with water. In other words, water will transfer to the non-image areas but not to the greasy image areas. The result is a printing surface which will pick up ink in a pattern and transfer the pattern to some other surface, and yet all portions of the printing surface are substantially level or plane, i. e. are without raised or intaglio areas.

For satisfactory performance the non-printing or blank areas of the plate must present a continuous aqueous film, and the quantity of aqueous fluid retained on the surface of the non-printing areas should not vary from the beginning to the end of a run of printing. During printing the plate is wet by a roller which applies water or "etching" or "fountain" solution to the non-printing areas and then by ink by another roller which applies ink to the image or printing areas. Accordingly, when a blank or clear sheet has been pressed against the inked plate, the ink which is on the image areas will come off onto the paper while the areas in contact with the non-image areas will remain clear since these areas of the plate are wet only with water and have no ink on them. When transferred to a clear sheet as described, the image is in reverse and if it is in writing or printing is not readily readable; accordingly, it is customary to employ off-set printing machines in which the image is first transferred to a blanket which receives the image in reverse, after which the blanket is brought in contact with the clear sheet which receives the image unreversed.

To understand the present invention it is necessary also to understand some of the many problems which have been encountered in the

2

past by those who have attempted to make paper base planographic plates. These problems and the background will now be reviewed.

If ordinary inexpensive paper, such as kraft, is used as a base, it swells and changes dimensions if the water or fountain solution penetrates the surface coating and reaches this base. This results in distortion of the image and in imperfect registration.

If the aqueous fountain solution works into the body of the plate, the surface of the plate may become less completely wetted by water because water has been withdrawn from the surface into the plate. Therefore, the surface may not repel the printing ink, and areas of the surface which should be perfectly blank will darken or "tone."

If a colloidal coating is present as a final surface, and if water penetrates that surface and renders the surface under the greasy image soluble, the image no longer will hold onto the plate and tends to fall or "walk-off" the printing surface. If, on the other hand, the surface is so highly resistant to grease that the imaging material fails to adhere properly the same thing takes place. The material forming the image must adhere tenaciously to the plate and not come off wholly or in part or be destroyed little by little by the successive transfer of the ink from the imaged areas.

These difficulties are particularly great with plates which are used for long runs and are therefore subjected to repeated wettings and inkings. Attempts have been made to overcome these difficulties by interposing a resinous water barrier between the paper base and the surface coating but this does not prevent the water being drawn from the surface into the coating layers above the barrier surface. The use of a barrier coating also involves the expense of the barrier layer so that this expedient is not practical nor satisfactory, particularly with low cost plates.

Several other difficulties also occur. Unless both sides of the plate are coated with a water-impervious barrier, curling during storage, or on wetting-out or after running may occur because the two sides of the plate are not in moisture balance. Fingerprints and accidental inkspots on the plate cannot be removed easily, if at all, and are reproduced on the blank sheet. Erasures from the plate cannot be made, or if made, require the use of liquid. The plates may deteriorate rapidly with age. There is often a tendency of the ink to emulsify and the printing to lose its sharpness and definition. Complicated techniques may be required in the treatment and

handling of the plates. Treatment before being put on the press may be required and the first few copies from the plate may be faint until the fountain solution and ink rollers have passed over the plate several times, resulting in waste of paper and loss of time. Special typewriter ribbons or pencils are required.

Many of the difficulties experienced in the past with paper base planographic printing plates result from the fact that surfaces which accept grease and ink satisfactorily are too easily penetrated by water or the fountain solution and consequently "tone-up" quickly giving the plate a short life and unsatisfactory printing characteristics. To be satisfactory the surface of the plate must be capable of being completely and uniformly wet with water or the fountain solution but must not be penetrated to any great extent during the life of the plate. Likewise the plate must be capable of retaining tenaciously the greasy image-forming material but the ink from the rollers must not be retained by or penetrate non-image bearing areas.

Accordingly, a primary object of the present invention is to provide a paper base coated planographic printing plate which will make a number of clear, sharp impressions; which can be made cheaply and economically by ordinary paper mill procedure; which will not "tone-up" during use; whose images will not fall off during use; which will permit the removal of finger marks, ink smears and the like; which will permit erasure without the use of liquids and without showing the erasure; which will not curl and may be stored in filing cabinets without deterioration and, therefore, will be capable of re-use after storage; and which will not require preliminary treatment before use on the press and when used will immediately produce commercially acceptable copies.

Another object of the present invention is to provide new and improved methods of making the new planographic printing plates.

Another object of the invention is to make it possible to omit the underlying barrier coat which has been previously employed to prevent the penetration of water into the paper base and thereby make it possible to produce a plate which will be satisfactory for many purposes by applying a single coat of material to the paper base.

My invention contemplates and includes within its scope treatment of the hydrophilic planograph image-receptive printing surface, as hereinafter defined, with a solution of a water-soluble, water-stable bivalent metal salt or the inclusion of such a salt therein in such a way that satisfactory plates are produced without employing a resinous water barrier, or, if one is used, plates are produced having extremely long life and other greatly improved characteristics. My invention, therefore, makes it possible to produce short run, medium run or long run plates with substantially no difference in processing or composition. A long run plate embodying my invention has produced more than 12,000 copies, while short run plates will produce more than 300 copies.

Accordingly, in practicing my invention, I provide a paper base sheet with a printing surface which includes finely divided mineral particles and a hydrophilic image-receptive material, modified by or including a water-soluble bivalent metal salt which is stable in water solution.

The water-soluble, water stable bivalent metal salt may be deposited as such from an aqueous solution thereof which does not contain any material which reacts chemically with the salt or in the form of the compound or compounds of the metal which are deposited by evaporation of an aqueous solution in which the salt has been reacted with ammonium hydroxide.

The exact nature of the effect of the water-soluble bivalent metal salt on the printing surface is not fully understood, but I do know that it increases the capacity of the surface to be wet by water or the fountain solution, while at the same time it decreases the penetration of the printing surface by the fountain solution or by grease and does not interfere with the capacity of the surface to receive and retain the substance composing the image, and I believe that this results because the water-soluble and water-stable bivalent metal salt tends to enter and to fill or plug up interstices, that is, the capillary pores of spaces, in or among the finely divided mineral particles and colloid embodied in the coating, particularly when a wetting-out solution is used which reacts with the bivalent metal salt to produce a bulky precipitate.

The bivalent metal salt increases the wettability of the image-receptive and printing surface of the plate for aqueous solutions while at the same time increasing the resistance to penetration by water after the application of the ordinary wetting-out solutions, and also produces a surface which has satisfactory stability on aging.

In any event, I have found that the water-soluble and water-stable bivalent metal salt component of the printing surface of coated paper base planographic printing plates made in accordance with the present invention so modifies the printing surface thereof that the new planographic printing plates possess the desirable properties and characteristics hereinbefore mentioned including significantly greater resistance to penetration by both grease and water than is possessed by comparable prior coated paper base planographic printing plates and I do not, therefore, limit myself to any exact explanation of the phenomena involved, whether they be chemical or physical or partly chemical and partly physical.

Having thus generally indicated the nature of coated paper base planographic printing plates made in accordance with the present invention, and their advantages, a detailed description of the method of making the new coated paper base planographic printing plates will now be given. The method employed in making the so-called medium run plate, which is intended to afford up to approximately a thousand copies, will first be described, after which there will be described those modifications of the general method employed in preparing the medium run plate which are necessary to adapt the method for use in preparing the short run plate, which is adapted to afford up to approximately two hundred copies, following which there will be described those modifications of the general method which are necessary to adapt the method for use in preparing the long run plate which is intended to afford five thousand or more copies.

MEDIUM RUN PLATE

Example 1

Step 1.—While any paper base sheet having sufficient wet strength to stand up during processing and in use may be employed as the paper base sheet in preparing planographic printing plates in the practice of the present invention, a typical suitable paper base sheet for use in pre-

paring the new paper base planographic printing plates may be prepared as follows:

A wet strength paper web of approximately 70 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 soda pulp and sulphate or bleached kraft, rosin-size, melamine-formaldehyde resin, and alum. The formed web is then preferably but not necessarily surface sized with a water solution of ammoniacal casein made slightly acidic by the addition of a water solution of formaldehyde. Between one and two pounds (dry weight) of the casein sizing material, per ream, should be taken up. The web may then be dried and machine-calendered. In place of a part or all of the sulphate pulp, sulphite pulp may be used and clay or other suitable filler, although not particularly desirable, may be included in the furnish.

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.

While the use of the melamine-formaldehyde resin in the furnish or the use of the casein-formaldehyde wash, referred to in the foregoing Step 1, will, separately, provide a paper base sheet which has fairly good wet strength and may be employed as the paper base sheet in making medium run planographic printing plates according to the present invention, a highly satisfactory paper base sheet for the new medium run planographic printing plates is provided by employing the melamine-formaldehyde resin in the furnish and also subsequently employing the casein-formaldehyde wash.

Step 2.—A paper base sheet or web prepared in the manner set forth in the foregoing Step 1 may be coated on each side thereof 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 1 so as to provide the pigmented hydrophilic base coat of the printing surface embodied in the new medium run plates:

Formula 1

	Parts by weight
Pigment (clay) (finely divided)	100.0
Hydrophilic adhesive base (casein) (in a water solution of ammonia)	17.5
Dimethylolurea urea (to insolubilize the casein)	1.75

The paper base sheet or web having the pigmented hydrophilic adhesive base coat of the foregoing Formula 1 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 15 minutes, and calendered, although calendering is not entirely essential.

Step 3.—The thus coated and calendered paper base sheet may then be washed on one side thereof, at room temperature, with a hydrophilic planographic image-receptive material in the form of a solution of a hydrophilic colloid coating having substantially the composition set forth in the following Formula 2 so as to provide the body of the outer coating which is embodied in the printing surface of the new medium run paper base planographic printing plates:

Formula 2

	Parts by weight
Planographic image-receptive hydrophilic material (sodium alginate)	1
Water	95
Butanol	4

The butanol in the composition employed in Formula 2 of the foregoing Step 3 decreases the foaming of the composition and facilitates penetration of the hydrophilic colloid (sodium alginate) into the capillary spaces, that is, the interstices or pores among the finely divided mineral particles of the clay pigment in the pigmented hydrophilic adhesive or of the clay-casein base coating.

Step 4.—The thus coated surface of the paper base sheet may then be washed, at room temperature with a composition having substantially the following formula:

Formula 3

	Parts by weight
(Water-soluble, water-stable bivalent metal salt.)	
Zinc acetate $Zn(C_2H_3O_2)_2.2H_2O$ (commercial)	25
Water	72
Butanol	3

If desired, though less satisfactorily, the sequence in which the planographic image-receptive material of Formula 2 (sodium alginate) and the bivalent metal salt solution of Formula 3 (zinc acetate) are applied may be reversed and the bivalent metal solution applied directly to the base coat of Formula 1 and the hydrophilic material (sodium alginate) then applied thereover.

Step 5.—The thus coated and treated paper base sheet was then dried and the face of the printing surface was thereupon rubbed against rotating brushes. While not essential to or indispensible 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 thus treated plates. Moreover, this operation of rubbing or brushing the face of the printing surface of the new paper base planographic printing plates tends to remove any excess of the bivalent metal salt which may crystallize on the surface of the plate; it greatly increases the resistance of the thus treated printing surface of the new planographic printing plates to fingerprints and ink smears; and it enhances the ease with which such fingerprints and ink smears may be removed from the printing surface of the plates by means of an aqueous planographic etching and dampening solution, or by means of an aqueous planographic repellent fountain solution while, at the same time, increasing the resistance of the printing surface of the new planographic printing plates to penetration by both grease and water.

The improvement in paper base planographic printing plates which resides in passing the printing surface of the plates against rotating brushes, or otherwise rubbing or brushing the printing surface of such paper base planographic printing plates forms the subject matter of the copending application of Frederick H. Frost, Serial No. 691,654, filed August 19, 1946, now aban-

doned, on "Paper Base Planographic Printing Plate," 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 the composition referred to in Formula 3 under Step 4 above, while not entirely essential in the practice of the present invention, facilitates and promotes penetration of the water-soluble, water-stable bivalent metal salt (zinc acetate) solution into the capillary spaces formed by the pores or interstices among the finely divided mineral particles in the clay-casein base coating, which imparts to the printing surface of the new coated paper base planographic printing plates the advantages and desirable characteristics hereinbefore referred to. In place of butanol, equivalent volatile water-miscible solvents including ethanol, methanol, propanol, and the like may be used in equivalent concentrations.

While it is possible, within the scope and contemplation of the present invention, to employ the sodium alginate solution of Formula 2 in Step 3 and the zinc acetate solution of Formula 3 in Step 4 in a single solution, the two materials are incompatible unless the solution is strongly ammoniacal, and it is preferred to employ these two solutions separately and in two separate steps when practicing the present invention according to the two-step coating phase thereof hereinbefore described. When thus employed the preferred concentration of the sodium alginate in the solution of Formula 2 in Step 3 is from not substantially less than 0.25 percent to not substantially more than 2.0 percent of the solution, by weight, and the preferred concentration of the zinc acetate in the solution employed in Formula 3 of Step 4 is from not substantially less than 5.0 percent to not substantially more than 30.0 percent of the composition, by weight, with an optimum percentage of about 20.0 percent, the zinc acetate being calculated as anhydrous zinc acetate.

The clay-casein ratio in the clay-casein base coat referred to in the foregoing Formula No. 1 may be varied widely from 12 to 100 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 per side of paper.

In place of the clay-casein base coating referred to in Formula No. 1, and which may be employed in the practice of the present invention according to the foregoing Example No. 1, other suitable pigmented hydrophilic adhesive base coatings which may be employed in the practice of the present invention according to the two-step coating phase thereof set forth in the foregoing Example No. 1, as well as according to the single step coating phase of the present invention which is set forth hereinafter in Example No. 2 are the following hydrophilic adhesive base materials: glue, gelatine, soya bean protein, zein, insolubilized starch, polyvinyl alcohol, gum arabic, or any other equivalent hydrophilic adhesive base material which may be pigmented and rendered highly resistant to penetration by both grease and water by means of a water-soluble, water-stable bivalent metal salt embodied in the printing surface of a paper base planographic printing plate, while still remaining hydrophilic.

Moreover, the clay or pigment component of the pigmented hydrophilic adhesive or clay-casein base coating referred to in the foregoing Formula No. 1 may be replaced in whole or in part by other suitable finely divided mineral pigments including barium sulphate, calcined clay, such as "Satintone" clay, talc, satin-white, titanium dioxide and other equivalent finely divided mineral pigments.

Other water-soluble hydrophilic colloids which may be employed in place of sodium alginate as the hydrophilic planographic image-receptive outer coating material and in place of the sodium alginate employed in Formula 2 of Step 3 above, and which may be employed with the zinc acetate solution of Formula 3 of Step 4, so as to impart the desired characteristics hereinbefore referred to, to the printing surface of the new paper base planographic printing plates, are the water-soluble hydrophilic colloidal materials referred to in the following Table 1:

Table 1

(1)

Gums:
- Arabic
- Mesquite
- Karaya
- Locust bean
- Guar (and similar mannogalactans similar to "Guar" gum)
- Ammonium Alginate

(2)

Proteins:
- Casein
- Soya bean protein
- Zein
- Glue (animal)
- Gelatin
- Albumin (egg)
- Albumin (blood)

(3)

Synthetic hydrophilic colloidal materials:
- Carboxy methyl cellulose
- "Rhotex" size (sodium polyacrylate)
- "Stymer" (a carboxy derivative of polystyrene rendered soluble by the addition of a suitable alkali such as caustic soda)
- Methyl cellulose
- Hydroxy ethyl cellulose "Cellosize"
- Polyvinyl alcohol

(4)

Other suitable hydrophilic colloidal materials:
- Starch
- Dextrin
- Pectins and derivatives thereof including fibrous sodium pectate

Thus in place of and as a substitute for the sodium alginate referred to in Formula 2 of Step 3 above I may substitute and I have used in making planographic printing plates according to the present invention each of the following materials in the percentages indicated, with sufficient water and butanol, in the ratio indicated in Formula 2 of Step 3, to make 100 parts of the solution:

	Percent by weight
Gum arabic	1 to 10
Mesquite gum	10
Karaya gum	0.5
Locust bean gum	0.2 to 1
"Guar" gum	0.2 to 1
Ammonium alginate	0.5 to 2
Casein	1 to 10
Soya bean protein	1 to 5
Zein	1 to 5

	Percent by weight
Glue (animal)	0.5 to 2
Gelatin	0.5 to 2
Albumin (egg)	5 to 10
Carboxymethyl cellulose	0.5 to 1.5
"Rhotex" size (sodium polyacrylate)	0.5 to 2
"Stymer" (a carboxy derivative of polystyrene rendered soluble by the addition of a suitable alkali such as caustic soda)	1
Methyl cellulose	0.5 to 2
Hydroxy ethyl cellulose	0.5 to 5
Polyvinyl alcohol	5
Starch	1 to 10
Dextrin	1 to 10
Sodium pectate (fibrous)	0.2 to 1.5

If desired, compatible mixtures of the hydrophilic colloidal materials referred to immediately above and in Table 1 may be used.

In the use of the hydrophilic colloidal materials referred to immediately above, as the outer coating of the printing surface of the new paper base planographic printing plates, the outer face of each of the thus coated paper base sheets or webs was washed with a fifteen (15) percent solution of zinc acetate in water and butanol in substantially the same ratio indicated in Formula 3, above, whereupon each of the sheets or webs was then dried and passed against rotating brushes as set forth in Step 5 of the foregoing Example No. 1.

In place of and as a substitute for zinc acetate as the water-soluble, water-stable bivalent metal salt component of the solution set forth in Formula 3, above, I have successfully employed each of the water-soluble bivalent metal salts referred to in the following Table 2 for the same purpose and in the concentrations indicated, all of the following water-soluble bivalent metal salts being sufficiently stable in water solution to enable them to be used in the practice of the present invention, and the water and butanol being present relative to each other in the solution in approximately the same ratio as in the foregoing Formula 3:

Table 2

	Percent by weight
Barium acetate	5 to 20
Barium nitrate	5 to 20
Cadmium acetate	5 to 20
Calcium acetate	5 to 20
Calcium chloride	5 to 25
Calcium formate	5 to 15
Calcium nitrate	5 to 25
Cobaltous acetate	5 to 20
Cobaltous chloride	5 to 25
Cobaltous nitrate	5 to 25
Cupric acetate (hot)	5 to 15
Cupric nitrate	5 to 25
Cupric sulphate	5 to 20
Ferrous sulphate	5 to 20
Lead acetate	5 to 20
Lead nitrate	5 to 25
Magnesium acetate	5 to 20
Magnesium chloride	5 to 25
Manganous acetate	5 to 20
Manganous nitrate	5 to 20
Manganous sulphate	5 to 20
Mercuric chloride	5 to 20
Nickelous acetate	5 to 15
Nickelous sulphate	5 to 20
Strontium acetate	5 to 20
Strontium nitrate	5 to 20
Zinc chloride	5 to 25

While all of the water-soluble bivalent metal salts referred to in Table 2 above are sufficiently stable in water solution to enable them to be used as the modifying agent in and for the printing surface of the new coated paper base planographic printing plates, and all of them have been successfully so used, I prefer to use the acetates of the bivalent metals in place of the other salts of bivalent metals referred to in Table 2 because the acetates are readily soluble in water, they are sufficiently stable in water, and they are readily controlled under manufacturing conditions.

If desired, mixtures of the bivalent metal salts of Table 2 which are compatible with each other may also be used.

While they may be used in the practice of the present invention, several of the water-soluble bivalent metal salts referred to in the foregoing Table 2, namely, the manganous salts, ferrous sulphate, and mercuric chloride, are inclined to be somewhat unstable in water solution, especially over prolonged periods of time, and hence are less suitable for use in the practice of the present invention than the other water-soluble bivalent metal salts listed in Table 2 and which possess sufficient stability in water solution to enable them to be used in actual manufacture of the new coated paper base planographic printing plates.

It will be noted, in this connection, that the preferred percentage of the water-soluble, water-stable bivalent metal salt which should be employed in the modifying solution of Formula 3 in Step 4, above, depends, in part, upon the particular method of coating and the apparatus employed in manufacturing the new coated paper base planographic printing plates and may be varied somewhat in accordance therewith. Thus, for example, if the so-called "air brush" method of coating is employed a somewhat higher concentration of the water-soluble, water-stable bivalent metal salt is preferable in the water solution thereof than is necessary when an ordinary brush coater is employed.

In applying the bivalent metal salt solution of Formula 3, or any of the other bivalent metal salts of Table 2, or mixtures thereof, either before or after the application of the hydrophilic colloid, the bivalent metal salt solution is preferably maintained within a range of from one-half gallon to five gallons per ream. Thus, for example, good results are obtained when approximately two gallons of bivalent metal solution are applied to sufficient base coated paper stock to form, when cut to size, a ream of 500 sheets or plates 25 x 38 inches.

Moreover, it is important in the practice of the present invention that the concentration of the water-soluble, water-stable bivalent metal salt in the water solution thereof be maintained substantially constant under manufacturing conditions and that the drying cycle employed in making the new paper base planographic printing plates treated with the water-soluble, water-stable bivalent metal salt solution be so adjusted as to enable the water-soluble, water-stable bivalent metal salt to penetrate well into the printing surface of the plates before the said bivalent metal salt solution dries since otherwise there is apt to be an excessive concentration, or even crystallization, of the bivalent metal solution upon the outer portions of the printing surface of the new planographic printing plates with resultant image failure in the use of the plates.

The temperature at which the water-butanol solution of zinc acetate may be employed as in Formula 3 and Step 4 above, and the temperature at which a corresponding water solution of a water-soluble, water-stable bivalent metal salt selected from Table 2, above, may be employed in making planographic printing plates according to the present invention, depends in part upon the method of coating employed although, in general, a water solution of any of these bivalent metal salts may be applied at ordinary temperatures, that is, atmospheric temperature.

By reference to the foregoing Table 2 it will be noted that this table includes representative water-soluble, water-stable salts of bivalent metals selected from groups 1—2—4—7 and 8 of the periodic table (Mendelejeff) and that while group 6 of the periodic table includes chromium, which forms a bivalent series of salts, such, for example, as chromous chloride ($CrCl_2$) this bivalent series of chromous salts are unstable in that, in the presence of air, they are readily oxidized to chromic salts and chromic acid with the intermediate formation of unstable compounds. Thus I have found that all water-soluble salts of bivalent metals selected from groups 1—2—4—7 and 8 of the periodic table, and which are sufficiently stable in water solution, regardless of the particular one of the said groups in the periodic table in which the metal component of the salt may be classified, are useful as and may be used as the modifying agent in the printing surface of coated paper base planographic printing plates made in accordance with the present invention, whereas such water-soluble bivalent metal salts, as the chromous salts, which are soluble in water solution, but which are unstable in water solution and tend to oxidize to the chromic condition, or to decompose in various ways, are unsuitable for use as the modifying agent in the printing surface of planographic printing plates made in accordance with the present invention. Moreover, I have also found that water-soluble salts of trivalent metals which are stable in water solution, such as some of the salts of trivalent metals selected from group 3 of the periodic table as, for example, trivalent aluminum, as exemplified by aluminum chloride ($AlCl_3$), are unsatisfactory particularly in that the printing surfaces of coated paper base planographic printing plates having any of such water-soluble trivalent metal salts incorporated therein lacks stability upon aging and when stored for prolonged periods of time prior to use. Likewise, I have found that the water-soluble, water-stable salts of monovalent metals do not have the desired modifying effect upon the printing surface of paper base planographic printing plates which is afforded by the water-soluble, water-stable bivalent metal salts employed in the practice of the present invention.

In making the various possible substitutions for the sodium alginate of Formula No. 2 from Table 1 and in selecting from Table 2 a suitable water-soluble, water-stable bivalent metal salt to be used in Formula No. 3 in place of the zinc acetate therein specified, it is desirable to select a hydrophilic colloid or other hydrophilic planographic image-receptive material and a water-soluble, water-stable bivalent metal salt which are compatible with each other in all proportions without the need for or use of any additional material. However, if in some cases and in certain proportions a certain degree of apparent incompatibility may arise between the selected hydrophilic colloid or other hydrophilic planographic image-receptive material and the selected water-soluble, water-stable bivalent metal salt such apparent incompatibility may be overcome by the addition of a suitable solubilizing agent for the selected combination so as to temporarily sequester the metal ion of the salt until the hydrophilic colloid or other hydrophilic planographic image-receptive coating composition and the water-soluble, water-stable bivalent metal salt solution have been applied to the pigmented hydrophilic adhesive base coat and dried. Thus, for example, when a selected one of the water-soluble, water-stable bivalent metal salts in Table 2 is mixed with sodium alginate of Formula No. 2, or with ammonium alginate, or with one of the proteins (casein, soya bean, zein, glue, gelatin and albumin) or with carboxy methylcellulose, sodium polyacrylate ("Rhotex" size), or "Stymer" from Table 1, some jelling takes place but this may be overcome and the materials rendered compatible by the addition of sufficient ammonia to render the mixture ammoniacal. However, these are the only instances of apparent incompatibility which have been found in making various combinations of materials from Tables 1 and 2 and, as above stated, they are overcome by the addition of ammonia. It may also be added that the use of ammonia for this purpose is particularly effective when a water-soluble, water-stable copper or zinc salt is employed with the selected hydrophilic colloid or other hydrophilic planographic image-receptive material.

An additional coating composition suitable for use in the two-step process may be prepared as follows.

Pectate pulp was prepared according to the following formula:

Formula No. 4

	Grams
Pectate pulp (dry) (No. 121, California Fruit Growers Exchange)	20
Sodium carbonate	2
Water (boiling)	440

In preparing the pectate pulp or sodium pectate according to Formula No. 4, above, dry sodium carbonate was mixed uniformly with the dry pectate pulp and the mixture was then added to the boiling water and boiled for ten minutes. The dispersion thus formed was then allowed to stand overnight at which time it showed some jelling. It was then warmed and diluted with cold water to a concentration of one percent whereupon the insoluble portion of the product was removed by straining through cheesecloth. The approximately one percent sodium pectate solution thus prepared was then applied to a suitable clay-casein base coated sheet prepared as in Formula No. 1, whereupon the sheet thus treated was dried for five minutes at 85° C. The sheet was then washed with a 16 percent solution of zinc acetate (calculated as anhydrous zinc acetate), dried and rubbed. The planographic printing plate thus prepared gave excellent results which were comparable to the results obtained in the use of the plate obtained in the use of Formula No. 3 above.

Other examp'es of pectins and pectates which may be employed in place of the sodium pectate prepared in the manner set forth in the foregoing Formula No. 4 are disclosed in United States Patent No. 2,287,849, dated June 30, 1942.

EXAMPLE 2

While the application of the outer coating of a hydrophilic planographic image-receptive material to the pigmented hydrophilic adhesive base coat, and the application of the water-soluble, water-stable bivalent metal salt solution thereto, in two separate and successive steps, as in the foregoing Example No. 1, provides satisfactory coated paper base planographic printing plates made in accordance with, and within the scope and contemplation of, the present invention, I prefer to apply the hydrophilic planographic image-receptive outer coating and the water-soluble, water-stable bivalent metal salt solution to the pigmented hydrophilic adhesive base coat in and as a single coating composition and as a single step. This single step process has certain distinct advantages over the two-step process of Example No. 1 including the fact that it makes possible better control in actual manufacture and eliminates the necessity for forcing the bivalent metal salt solution down through the previously applied and underlying outer coating of a hydrophilic colloid or like hydrophilic planographic image-receptive material as is necessary in employing the two-step process of Example No. 1 when the bivalent metal salt solution is applied subsequent to the hydrophilic colloid or like material in the two-step process of Example No. 1. Thus I have found that the new coated paper base planographic printing plates may be advantageously prepared and the printing surface thereof suitably formed and modified by applying the hydrophilic colloid or equivalent hydrophilic planographic image-receptive material and the bivalent metal salt solution to the pigmented hydrophilic adhesive base coat, previously applied to the paper base sheet, in and as a single coating composition and as a single step or coating operation.

A suitable paper base sheet, which may be a paper base sheet such as that referred to in Example No. 1, is first provided with a suitable pigmented hydrophilic adhesive base coat, which may be the clay-casein base coat of Formula No. 1, or other equivalent pigmented hydrophilic adhesive base coating, dried as, for example, at a temperature of 120° F. to 140° F. for a period of from 10 to 15 minutes. Over the thus dried pigmented hydrophilic adhesive base coating there may then be applied an outer coating comprised of a hydrophilic colloid, or other equivalent hydrophilic planographic image-receptive material, such as a selected one of the suitable materials hereinafter referred to, and a water-soluble, water-stable salt of a bivalent metal which may be a selected one of the water-soluble, water-stable bivalent metal salts referred to in the foregoing Table 2.

Thus a suitable one-step hydrophilic colloid water-soluble, bivalent metal salt coating composition may be prepared according to the following formula:

Formula No. 5

	Parts by weight
Hydrophilic colloid (1.25 percent "Guar" gum in water—0.22 percent dry "Guar" gum in the batch	8.95
Water solution of formaldehyde (40 percent of HCHO)	1.75
Silica aquasol "Syton W20"—Monsanto (also known as "Meritone W") (15 percent water dispersion)	[1] 1.33

[1] 0.2 part dry weight.

	Parts by weight
Water solution of zinc acetate (25 percent $Zn(C_2H_3O_2)_2$	[2] 33.40
Butanol	1.50
Dye (water solution of Victoria green—0.22 percent	3.65
	50.58

[2] 7.0 parts anhydrous zinc acetate.

In applying the hydrophilic colloid-bivalent metal salt coating composition of Formula No. 5, above, or any selected substitute coating composition used in the one-step coating process of Example No. 2, the coating composition is preferably maintained within a range of from one-half gallon to five gallons of the coating composition applied to sufficient base coated paper stock to form, when cut to size, a ream of 500 sheets or plates 25 x 38 inches. Thus, good results are obtained when two gallons of the coating composition are employed, per ream, as defined. Thus, a typical coating composition comparable to the foregoing Formula No. 5 was maintained in the one-step process of Example No. 2 at two gallons per ream, as defined, and contained 0.25 percent of "Guar" gum, 15 percent zinc acetate (calculated as anhydrous zinc acetate), and 0.4 percent of silica aquasol "Syton W20." This coating composition had a specific gravity of 1.1.

The hydrophilic colloid-water-soluble, water-stable bivalent metal salt coating composition of the foregoing Formula No. 5 may be applied in a single step at room temperature over the pigmented hydrophilic base coating by means of any suitable coating apparatus and allowed to dry whereupon the printing surface of the thus coated paper base sheet is preferably, but not necessarily, rubbed by passing the coated paper base sheet or web against rotating brushes. While not essential to or indispensable in the manufacture of the new coated paper base planographic printing plates according to that phase of the invention which is represented by the present Example No. 2, this rubbing operation, as described in Step 5 of Example No. 1, has certain desirable advantages among which are that it tends to remove any excess of the bivalent metal salt which may crystallize on the surface of the plate; it greatly increases the image-reproducing life of the plates; and it improves the quality of the images reproduced from the thus treated plates. Moreover, this operation of rubbing or brushing the face of the printing surface of the new paper base planographic printing plates increases the resistance of the hydrophilic colloid outer coating on the paper base sheet to fingerprints and ink smears and its ability to retain both ink and water upon its outer surface while, at the same time, increasing the resistance of the outer hydrophilic colloid coating to penetration by grease and water.

In the manufacture of the new paper base planographic printing plates employing the single step outer coating composition of the foregoing Formula No. 5, or any of the equivalent single step outer coating compositions hereinafter referred to, it is important that the rate of drying of the applied coating composition be so controlled as to permit adequate penetration of the coating into the base coating. This is for the reason that if the applied coating does not have sufficient time to penetrate into the base coating before drying a tendency may develop for the water-soluble and water-stable bivalent metal salt to crystallize out of solution and cause an undesirable increase in the concentration of the

water-soluble and water-stable bivalent metal salt upon the printing surface of the plate which will be manifested by rapid loss of the greasy planographic image on the finished plate under normal conditions of use. For the same reason care must be taken to maintain the concentration of the various components of the coating composition substantially constant during the coating operation.

The hydrophilic colloid referred to in the foregoing Formula No. 5, namely, "Guar" gum is a vegetable gum originally from India but now available upon the American market (General Mills) and is probably a manno-galactan. The concentration of this material employed in the foregoing Formula No. 5 may be varied between 0.05 and 1.25 percent, inclusive, by weight, of the coating composition calculated as dry "Guar" gum.

The silica aquasol, referred to in the foregoing Formula No. 5 ("Syton W20," also known as "Mertone W"), is available upon the market (Monsanto Chemical Co.) and the composition thereof and its preparation are disclosed in United States Patent No. 2,375,738. The silica aquasol component of the composition of the above Formula No. 5 may be varied from 0.05 to 2.0 percent, inclusive, of the composition, dry weight. The use of the aforesaid silica aquasol in the single step outer coating composition of the foregoing Formula No. 5 facilitates the removal of fingerprints and ink smears from the printing surface of the resulting planographic printing plates and while not indispensable it enhances this desirable property in the new planographic printing plates.

The use of a silica aquasol in the manufacture of coated paper base planographic printing plates forms the subject matter of and is claimed in the copending application of Stephen V. Worthen and Charles H. Van Dusen, Serial No. 788,660, filed November 28, 1947, and entitled "Planographic Printing," and hence no claim is herein made broadly to the use of said silica aquasol and this material is herein claimed only as it is embodied in the new coated paper base planographic printing plates of the present invention.

In preparing the hydrophilic colloid water-soluble and water-stable bivalent metal salt coating composition referred to in Formula No. 5, above, the hydrophilic colloid, the water solution of formaldehyde and the silica aquasol should be thoroughly mixed together, and the zinc acetate-butanol-dye solution prepared separately, whereupon the two solutions thus prepared separately should be mixed together.

The zinc acetate component of the coating composition of the foregoing Formula No. 5 may be varied from 5 to 25 percent, inclusive, of the complete coating composition, by weight, calculating the zinc acetate as the anhydrous zinc acetate $Zn(C_2H_3O_2)_2$. However, as hereinbefore indicated, the concentration of the zinc acetate in the coating composition of the foregoing Formula No. 5 may be varied somewhat depending upon the particular coating method and apparatus employed.

The quantities and concentrations of the water-soluble, water-stable bivalent metal salt, as employed in the foregoing Formulae Nos. 3 and 5, and in Tables 2 and 4 herein, provide an excess of the bivalent metal salt over and above any portion or amount thereof which is capable of reacting with the hydrophilic adhesive material (casein) in the base coating or with the hydrophilic organic material, such as the sodium alginate of Formula No. 2, or with certain of the other hydrophilic organic materials referred to in Tables 1, 3, and 4 herein. There is no observable reaction between the bivalent metal salt and certain of the other hydrophilic materials employed such as the "Guar" gum of Formula No. 5 or methyl cellulose, or the hydroxy ethyl cellulose, or the polyvinyl alcohol of Table 3 herein. But the quantities and concentrations of the bivalent metal salt, as hereinbefore set forth, allow for any possible reaction, and provide an excess of the bivalent metal salt over and above any amount thereof which may enter into any such reaction. I believe that this excess of bivalent metal salt reacts with one or more of the constituents of the wetting-out solutions, for instance, monoammonium phosphate, and produces a bulky precipitate wherever the bivalent metal salt has penetrated the base coating, and that this action explains the superior quality of the planographic printing plates made in accordance with my invention.

While not entirely essential, the butanol employed in the single step hydrophilic colloid-water-soluble, water-stable bivalent metal salt coating composition of the foregoing Formula No. 5 is helpful in effecting penetration of the coating composition into the capillary spaces, that is, into the pores or interstices, of the clay-casein base coating. In place of butanol other equivalent volatile materials may be employed in equivalent concentrations and among these are ethanol, methanol and propanol.

The use of the water-soluble green dye referred to in Formula No. 5 above is, of course, optional and other suitable water-soluble dyes may be employed if a colored planographic printing plate is desired or the dye may be eliminated entirely and a white planographic printing plate thus prepared.

In place of the particular hydrophilic colloid employed in the single step coating composition of the foregoing Formula No. 5, namely, "Guar" gum, other suitable hydrophilic colloids, and other suitable hydrophilic non-colloidal planographic image-receptive materials may be employed, and among these are the hydrophilic planographic image-receptive materials set forth in the following Table 3.

Table 3

Gums:
- Arabic
- Mesquite
- Karaya
- Locust bean
- (And other mannogalactans similar to "Guar" gum)

Synthetic hydrophilic colloidal materials:
- Methyl cellulose
- Hydroxy ethyl cellulose ("Cellosize")
- Polyvinyl alcohol

Other suitable hydrophilic colloidal materials:
- Starch
- Dextrin
- Pectins and derivatives thereof including fibrous sodium pectate

Hydrophilic non-colloidal materials (carbohydrates):
- Mannitol
- Sorbitol
- Sucrose
- Invert sugar
- Corn syrup
- Mannose

Thus, for example, certain of the hydrophilic planographic image-receptive materials referred to in the foregoing Table 3 may be substituted for the particular hydrophilic colloid specified in the foregoing Formula No. 5 in the concentrations set forth in the following Table 4 and with such variations in the concentration of the water-soluble, water-stable bivalent metal (zinc acetate) component of the single step outer coating composition as are indicated in the following Table 4 in which the zinc acetate is shown calculated as anhydrous zinc acetate.

Table 4

	Percent by weight
Gum arabic	4
and	
Zinc acetate	15
Mesquite gum	4
and	
Zinc acetate	15
Karaya gum	0.5
and	
Zinc acetate	15
Locust bean gum	1
and	
Zinc acetate	15
Starch	5
and	
Zinc acetate	15
Dextrin	5
and	
Zinc acetate	15
Sodium pectate (fibrous)	1
and	
Zinc acetate	16
Methyl cellulose	1
and	
Zinc acetate	15
Hydroxy ethyl cellulose	0.75
and	
Zinc acetate	15
Polyvinyl alcohol	5
and	
Zinc acetate	15
Mannitol	5
and	
Zinc acetate	15
Sorbitol	5
and	
Zinc acetate	15
Sucrose	5
and	
Zinc acetate	15
Glucose	5
and	
Zinc acetate	15
Invert sugar	5
and	
Zinc acetate	15
Corn syrup	5
and	
Zinc acetate	15
Mannose	5
and	
Zinc acetate	15

While the hydrophilic carbohydrates or sugars referred to in Tables 3 and 4, namely, mannitol, sorbitol, sucrose, glucose, invert sugar, corn syrup and mannose are not colloidal in nature, I have found that when employed with a selected one of the aforesaid water-soluble, water-stable bivalent metal salts as the base of the outer single step coating composition the coated paper base planographic printing plates having thereon the hydrophilic planographic image-receptive surface afforded thereby, and as modified by the water soluble, water-stable bivalent metal salt component thereof, have the desirable properties and characteristics hereinbefore referred to.

Any of the water-soluble, water-stable bivalent metal salts of Table 2, or compatible mixtures thereof, may be substituted in the foregoing Formula No. 5, in place of the zinc acetate therein specified or in place of the zinc acetate employed with the various hydrophilic materials referred to in Table 4 and which may be substituted for the particular hydrophilic colloids specified in Formula No. 5, namely, "Guar" gum. Similarly, if desired, compatible mixtures of the hydrophilic material referred to in Table 4 may be employed in place of the "Guar" gum specified in Formula No. 5. However, in making these various substitutions it is desirable to select a hydrophilic colloid or other hydrophilic planographic image-receptive material and a water-soluble, water-stable bivalent metal salt, or mixtures of these materials, which are compatible in all proportions without the need for or use of any additional material. However, if in some cases in certain proportions a certain degree of apparent incompatibility may arise between the selected hydrophilic colloid or other hydrophilic planographic image-receptive material and the selected water-soluble, water-stable bivalent metal salt, such apparent incompatibility may be overcome by the addition of a suitable solubilizing agent for the selected combination so as to temporarily sequester the metal ion of the salt until the said single step outer coating composition has been applied to the pigmented hydrophilic adhesive base coat and dried. Thus, for example, when karaya gum and zinc acetate are employed together in a single step coating composition otherwise comparable to the foregoing Formula No. 5 there is no jelling action but there may be some separation on standing unless the mixture is agitated but this may be overcome by making the mixture ammoniacal. However, the combination of karaya gum and zinc acetate may be employed in the single step outer coating composition, otherwise comparable to Formula No. 5, either with or without the addition of ammonia.

While the hydrophilic colloid water-soluble, water-stable bivalent metal salt single step outer coating composition of the above Formula No. 5 may be applied at room temperature in some instances better results may be obtained by applying the said single step hydrophilic colloid water-soluble, water-stable bivalent metal salt coating composition to the clay-casein or equivalent pigmented hydrophilic adhesive base coating as a hot solution since this procedure enhances penetration of the water-soluble, water-stable bivalent metal salt component of the said single step outer coating composition into the capillary spaces formed by the pores or interstices in the clay-casein or equivalent pigmented hydrophilic adhesive base coating and thus increases the resistance of the clay-casein or other pigmented hydrophilic adhesive base coating to penetration by grease and water.

SHORT RUN PLATE

Suitable so-called short run paper base planographic printing plates, for reproducing up to approximately two hundred copies, may be prepared within the scope and contemplation of the present invention by means of the two step outer coating process of Example No. 1 or by means of the single step outer coating process of Example No. 2, and by the use of the materials hereinbefore referred to, with such variations as are desirable and as are uncessary to reduce the cost of manufacturing the short run plate relative to the cost of manufacturing the medium run plate.

Thus, in preparing short run plates according to the present invention a paper base sheet may be prepared according to Step 1 in Example No. 1 above, but employing relatively cheaper fiber and omitting wet strength-imparting materials so as to reduce the cost of manufacture of the plate. Thus, in preparing the short run plates there may be omitted the operation of applying the casein-formaldehyde size or wash to the surface of the formed paper base sheet and the melamine-formaldehyde resin incorporated in the furnish, as in Step 1 of Example No. 1, may also be omitted.

In preparing the short run plate the casein content of the clay-casein base coating of Formula No. 1 in Example No. 1 may be increased to from 20 to 25 parts of casein per 100 parts of clay so as to provide increased resistance to water penetration in the clay-casein base coating which is desirable in view of the fact that the paper base sheet for the short run plate is not provided with the casein-formaldehyde wash employed upon the paper base sheet for the medium run plate.

LONG RUN PLATE

Long run coated paper base planographic printing plates, for use in preparing 5000 or more copies, may be prepared according to the practice of the present invention by following substantially the same process, and employing the same materials, as are used in preparing the medium run plates by either the two-step outer coating process of Example No. 1, or the single step outer coating process of Example No. 2, with such variations as are necessary to impart to such long run plates the additional resistance to water penetration required therein. Thus the long run plates must be provided with a water barrier and a suitable water barrier coating which may be employed may be prepared according to the following formula.

Formula No. 6

	Parts by weight
(1) "Butvar" (Monsanto) resin emulsion consisting of:	
(a) 100 parts polyvinyl butyral	15
(b) 40 parts of butyl ricinoleate (plasticizer)	
(c) 5 parts soap (emulsifier)	
(2) Clay	15
(3) Water	25

The resin emulsion and the clay in the above Formula No. 6 were calculated on the basis of their dry weight.

The water barrier coating referred to in the foregoing Formula No. 6 may be applied to the paper base sheet in such quantity as will provide a water barrier coating of suitable thickness and which may be effected by applying from 5 to 30 pounds of the composition of Formula No. 6 per ream of paper per side, with an optimum of 8 pounds per ream per side.

In place of the water barrier coating of Formula No. 6, above, other suitable water barrier coating compositions may be employed and among these are urea-formaldehyde resin, polyvinyl chloride ("Geon"), polymerized vinylidene chloride, ("Saran," Dow Chemical Co.), styrene polymers, various acrylates including "Rhoplex," and numerous resins of the elastomer type, and mixtures thereof.

At several points in the preceding discussion reference has been made to the efficacy of ammonia in promoting compatibility between bivalent metal salts and hydrophilic organic matter so that there can be combined in a single aqueous solution two components which otherwise would be incompatible, with consequent elimination of an otherwise necessary step in the process. Such ammoniacal aqueous solutions of bivalent metal salts, may also be included with beneficial results in aqueous pigment-adhesive coating compositions. A suitable coating composition comprises (1) a pigment or filler, such as clay or blanc fixe, (2) an organic adhesive, such as casein or glue, and (3) a solution of a bivalent metal salt, more particularly an ammoniacal solution of a bivalent metal salt which will first be precipitated by ammonia and then redissolved in excess ammonia. The coating differs from prior coatings in that comparatively large quantities of metal salt are employed; i. e. much more salt is used than can react with the adhesive. Comparison of following Examples 3 and 4 shows the beneficial effect given by inclusion of ammoniacal cupric chloride in a clay-casein coating composition.

EXAMPLE 3

Cupric chloride was dissolved in water to give a solution of 22 parts $CuCl_2$ in a total weight of about 60 parts. To this was added slowly and with a stirring concentrated ammonia water. Cupric hydroxide was first precipitated, and the addition of ammonia water was continued until the precipitate redissolved to give the characteristic deep blue color of cuprammonium solutions. This solution was then stirred into an ammoniacal solution of casein containing 22 parts of casein in 90 parts total. This in turn was added to a slip of 100 parts of Georgia coating clay in water, the final mixture having a solids content of about 35 per cent. Thus the copper salt used amounted to slightly over 15 percent of the total solids of the coating and was equal to the weight of the adhesive used. This coating mixture to the amount of 13 pounds dry weight per 500 sheets cut 25" x 38" was applied in conventional manner to one side of the body stock mentioned above. The so-coated paper was dried and calendered.

The sheet described above was typed upon with a typewriter using a record ribbon. The sheet was placed on the plate cylinder of an offset duplicating machine, swabbed over as is customary with an aqueous solution of glycerine and acidic phosphate, and then run in customary fashion as a lithographic printing plate. The quality of printing obtained therefrom was excellent. After 1,000 impressions had been made the printing was still of fine quality; and moreover the sheet had not become saturated with water at that time, showing that the coating acted both as a print surface and as an efficient water-barrier.

EXAMPLE 4

The procedure of Example 3 was repeated except that the ammoniacal copper solution was omitted. In this case the whole plate became solid black upon the first contact with the inking rollers, and the sheet was completely unusable as a printing plate. This example shows by contrast with Example 3, the importance and effect of the bivalent metal salt.

In place of the clay pigment and casein adhesive used in Example 3 any of the other pigments or fillers previously mentioned or any of the other hydrophilic adhesives previously referred to may be used in whole or in part. If desired, a mixture of adhesives may be used, or additional hydrophilic colloid may be added in small quantity to improve the hydrophilic characteristics of the coating. Enough adhesive must be used to bind the coating securely to the base. The absolute minimum that can possibly be used can be determined by experiment. As is well understood in the art, this minimum quantity will depend upon the inherent strength of the particular adhesive used, the particular filler used, the quality of body stock used, and the weight of the coating applied. In general the quantity of adhesive used will never be less than 10 parts to 100 of filler and preferably it will not be less than 15 parts per 100 of filler. Considerably more adhesive than the actual minimum required by strength may be advantageously employed, but too much adhesive introduces difficulties due to curling and the like. Consequently, 75 parts of adhesive to 100 of filler may be considered the extreme upper limit usable, while it is preferred not to exceed 50 parts per 100 of filler.

The weight of coating applied can be varied from between about 1 pound to about 8 pounds per thousand square feet of surface or between about 3 pounds and about 7 pounds per ream. The surface is preferably calendered, but not necessarily so.

It is apparent that bivalent metal salt used in ammoniacal solution must be a salt of a metal which will be soluble in excess ammonia. The bivalent metal salts which are most effective are those which when made alkaline by ammonia water, first form a precipitate of the hydroxide of the metal which upon further addition of ammonia water will be peptized or dissolved. Such salts include copper, zinc, cadmium, nickel, and cobaltous salts. When such ammoniacal bivalent metal salt solutions are used, either in a pigment-adhesive coating composition or as a wash applied to the surface of a coated paper sheet, it is probable that upon drying or evaporation while part of the metal salt may combine with the adhesive, e. g. casein, more of it undoubtedly exists in the surface coating as the metal hydroxide and some of it may perhaps exist as a metal-ammonium salt.

In any case, to be effective according to the invention much more of the ammoniacal solution of bivalent metal salt must be used than is capable of reacting with the adhesive or other organic hydrophilic matter present. This is well illustrated by following Example 5.

EXAMPLE 5

The procedure of Example 3 was repeated except that in place of the ammoniacal copper solution there was substituted an ammoniacal solution of zinc chloride equivalent to 66 parts of $ZnCl_2$. It will be understood that the zinc hydroxide at first precipitated had been redissolved by additional ammonia water. The results obtained were substantially identical with those of Example 3. It may be noted that in this case the quantity of anhydrous zinc salt used amounted to 35 percent of the total solids in the coating and was equal in weight to 300 percent of the weight of casein used.

In the preceding example (Example 5) the theoretical quantity of zinc chloride capable of reacting with the casein adhesive is not over 1.5 parts while actually 66 parts of zinc chloride dissolved in ammonia was used in the composition. Experiment showed, in compositions identical with that of Example 5 except for the quantity of ammoniacal zinc chloride used, that 11 parts of zinc salt (calculated as anhydrous $ZnCl_2$) was too little to be satisfactorily effective. Satisfactory results were obtained when the zinc salt present (calculated as anhydrous $ZnCl_2$) amounted to from about 15 to 42 percent of the total solids present in the coating composition.

Other specific examples follow showing application to coated paper surfaces of solutions of simple and ammoniacal salts of bivalent metals.

EXAMPLE 6

A sheet of wet-strength paper was coated on one side with a coating containing 100 parts of clay and 18 parts of casein dissolved by ammonia. About 15 pounds dry weight of coating was applied per 500 sheet ream of size 25" x 38". This coating was dried and calendered and then washed with a strongly ammoniacal solution to which 16 percent by weight of $ZnCl_2$ had been added. The sheet was dried and used as an offset plate. One thousand prints were made therefrom without objectionable wet-through of the plate. The printing quality was good.

EXAMPLE 7

The Example 6 above was repeated except that the ammoniacal zinc chloride wash was replaced by a wash of 20 percent lead acetate solution. Results were substantially equivalent to those of Example 6.

EXAMPLE 8

A sheet of wet-strength body stock was coated on one side with 3½ pounds per ream, dry weight, of a mixture of clay 100 parts, ammonium caseinate 35 parts, and mesquite gum 10 parts. The sheet was calendered and then washed with an 8 percent aqueous solution of zinc acetate. The sheet when dried and used as an offset plate was very resistant to water-penetration and printed well. The presence of the very hydrophilic mesquite gum was beneficial in this case.

From the foregoing examples it will be seen that the amount of the bivalent metal salt employed, whether in the form of the simple salt or in the form of an ammonium complex, must bear a definite relation to the amount of adhesive (casein or the like) contained in the coating, being always more than the amount which will react with the adhesive so that uncombined salt will be present and that when the upper and lower limits of the range already pointed out; i. e. 15 to 42%, are passed, the results are unsatisfactory. Also it will be appreciated that in applying aqueous solutions of bivalent metal salts to a coated paper surface, it is only necessary to apply an amount of the bivalent metal salt which is greater than the amount which will react with the adhesive content of the surface of the coat-

ing because only the surface of the pigment coating and not its entire depth is affected by the applied metal salt. Therefore a minute amount of the bivalent metal salt applied to the surface of the adhesive-pigment coating if it did not penetrate into the coating would exceed the amount required to react with the adhesive in or on the surface of the coating. The actual salt content of that portion of the coating containing it has not been determined, but from the study already described, it appears that the salt content effected by a surface treatment of the coating with salt solution will lie within the range of 15 to 42%.

By the terms "inert filler," "pigment," and similar terms, as used hereinafter in the claims, are meant those finely divided inert materials, including finely divided mineral fillers, such as clay and the like, hereinbefore referred to, which are commonly known and used as fillers or pigments in the arts of paper making and paper coating and which are incorporated in the hydrophilic adhesive base coating of the new paper planographic printing plates as finely divided inert fillers or mineral particles dispersed therethrough, even though such materials are not employed in the practice of the present invention for the purpose of imparting color to the new coated paper base planographic printing plates.

By the term "printing surface" as used hereinbefore and as used hereinafter in the claims, there is meant the dried product which is formed by the base coat comprised of a hydrophilic adhesive having finely divided mineral particles dispersed therethrough, and/or the outer coating of a hydrophilic material, the said printing surface containing and being modified by either the evaporation residue of a water-soluble bivalent metal salt which is stable in water solution or the evaporation residue of an aqueous ammoniacal solution of a complex ammonia-bivalent metal compound. It is to be understood, however, that the exact nature of the modifying effect of the said evaporation residues in said printing surface is not fully understood. Hence I do not, therefore, limit myself to any exact explanation of the phenamena thus involved and which may be chemical or physical or partly chemical and partly physical.

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

It will also thus be seen that the present invention provides new and improved compositions and processes for preparing the new coated paper base plantographic printing plates and that the invention thus accomplishes its intended objects including those hereinbefore pointed out and others which are inherent in the invention.

This application is a continuation of my applications Serial No. 747,138, filed May 9, 1947 (now abandoned) and Serial No. 758,215, filed June 30, 1947 (now abandoned), which are consolidated in this application.

I claim:

1. A planographic printing plate comprising a paper base and a planographic printing surface, said surface 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 of a water-soluble bivalent metal salt in excess of the amount capable of reacting with the adhesive material.

2. A planographic printing plate comprising a paper base and a planographic printing surface, said surface 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 bivalent metal compound of the group consisting of water-soluble, water-stable bivalent metal salts and the reaction products of ammonium hydroxide with water-soluble, water-stable salts of metals of the group consisting of copper, zinc, cadmium, nickel and cobalt.

3. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing a water-soluble, water-stable bivalent metal salt in excess of the amount capable of reacting with the adhesive material.

4. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing a water-soluble, water-stable bivalent metal salt of a metal selected from the group consisting of barium, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, strontium and zinc, said salt being in excess of the amount capable of reacting with the adhesive material.

5. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing zinc acetate in quantity in excess of the amount capable of reacting with the adhesive material.

6. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing lead acetate in quantity in excess of the amount capable of reacting with the adhesive material.

7. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing cobaltous acetate in quantity in excess of the amount capable of reacting with the adhesive material.

8. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing cupric acetate in quantity in excess of the amount capable of reacting with the adhesive material.

9. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing ferrous acetate in quantity

in excess of the amount capable of reacting with the adhesive material.

10. A planographic printing plate comprising a paper base and a planographic printing surface, said surface comprising insoluble hydrophilic adhesive material and finely divided inert mineral pigment, and having therein capillary interstices and pores containing hydrophilic organic material and a water-soluble, water-stable bivalent metal salt in excess of the amount capable of reacting with the hydrophilic material.

11. A planographic printing plate as defined in claim 10 in which the hydrophilic organic material is "Guar" gum.

12. A planographic printing plate comprising a paper base sheet having thereon a printing surface comprised of a hydrophilic adhesive base coating having finely divided mineral particles dispersed therethrough, and an additional coating of hydrophilic organic material, said printing surface containing a water-soluble and water-stable bivalent metal salt of a metal selected from the group consisting of barium, cadmium, calcium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, strontium and zinc, said salt being present in a quantity in excess of the amount capable of reacting with the hydrophilic material in the printing surface.

13. A planographic printing plate comprising a paper base sheet having in immediate contact therewith a planographic image-receptive, relative water-impermeable coating which contains finely divided particles of inert filler distributed through a hydrophilic adhesive, the surface portion at least of which coating contains and is modified by metal compound deposited in situ from an ammoniacal aqueous solution of a water-soluble, water-stable bivalent metal salt, the latter in quantity amounting to from 15 percent to 42 percent of the weight of that portion of the coating containing said metal compound.

14. A planographic printing plate comprising a paper base sheet having in immediate contact therewith a planographic image-receptive, relatively lithographic-solution impermeable coating which contains finely divided particles of inert filler distributed through a hydrophilic adhesive, the surface portion at least of which coating contains and is modified by metal compound deposited in situ from an ammoniacal aqueous solution of a water-soluble, water-stable bivalent metal salt, the latter in quantity in excess of the amount capable of reacting with the adhesive material.

15. The process for the production of a planographic printing plate which comprises coating a paper base sheet with a mixture of a hydrophilic adhesive material and finely divided mineral pigment resulting, when dried, in a surface having therein capillary interstices and pores, and incorporating in said surface a water-soluble, water-stable bivalent metal salt in a quantity in excess of the amount capable of reacting with the hydrophilic adhesive material.

16. The process defined in claim 15 in which the adhesive-pigment coating is dried and a solution of the salt is applied thereto.

17. The process defined in claim 15 in which the adhesive-pigment coating is dried and an aqueous mixture of the hydrophilic organic material and the metal salt is applied thereto.

18. The process defined in claim 15 in which the adhesive-pigment coating is dried, a hydrophilic organic material is applied to said adhesive-pigment coating, and a solution of the metal salt is applied to the resulting surface.

19. Process for the production of a planographic printing plate which comprises coating a paper base with a liquid coating composition consisting essentially of water, a hydrophilic adhesive, a finely divided inert filler and a complex ammonium compound of a bivalent metal of the group consisting of copper, zinc, cadmium, cobalt and nickel, said metal in the form of a water-soluble, water-stable simple salt amounting to from 15 percent to 42 percent of the sum of the dry weights of the filler and adhesive contents of the composition.

20. Process for the production of a planographic printing plate which comprises applying to the surface of a coating consisting essentially of a hydrophilic adhesive and a finely divided filler on a paper base, an aqueous ammoniacal solution of a complex ammonium compound of a bivalent metal of the group consisting of copper, zinc, cadmium, cobalt and nickel, said metal, in the form of a water-soluble, water-stable simple salt, amounting to from 15 percent to 42 percent of the dry weights of the filler and adhesive contents of the composition.

21. Process for the production of a planographic printing plate which comprises applying to the surface of a coating consisting essentially of a hydrophilic adhesive and a finely divided filler on a paper base, an aqueous ammoniacal solution of a complex ammonium compound of a bivalent metal in excess of the amount capable of reacting with the adhesive material.

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No references cited.