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COATED PAPER PLANOGRAPHIC PRINTING PLATE

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This invention relates to coated paper planographic printing plates suitable for producing printing runs in the order of from 10,000 to 100,000 copies.

Planographic printing is a form of lithographic printing which uses plates that are substantially plane, having image areas which are neither intaglioed nor raised above the adjacent surface. In use the blank or unimaged areas are kept wet with aqueous lithographic solution and so are ink-repellent. The imaged areas, being water-repellent, are not wet by the aqueous solution and so are free to accept ink from the inking-rolls of the printing-press, and when so inked can thereafter print the image in reverse on any ink-receptive surface brought into contact therewith. In practice the print is first made on a rubber offset blanket from which it is transferred to paper so that the final print is identical with the design on the plate.

Plates of metal, e. g. zinc or aluminum, having a surface roughened by abrasive or chemical treatment are satisfactory for use in planographic printing, but are expensive. At the present time coated paper planographic printing plates have largely replaced metal plates for use on small rotary offset duplicators, especially for making runs of not more than a few thousand. Such coated paper plates are considerably cheaper than metal plates; moreover, at least in the smaller sizes, they are more convenient to prepare for use. Usually, however, metal planographic printing plates can be expected to produce about 50,000 satisfactory prints; whereas in general it has not been possible to depend on coated paper planographic printing plates for more than about 10,000 prints.

The present invention contemplates a coated paper planographic printing plate, and a method of producing the same, of such a nature that said plate is capable of producing a large number of prints, approaching the number ordinarily obtainable from metal planographic printing plates.

Coated paper planographic printing plates, in general, comprise a paper base with a layer of coating thereon comprising finely divided mineral pigment and insolubilized hydrophilic organic adhesive material. Coated paper planographic printing plates hitherto commercially available have invariably to the best of our knowledge and belief, contained clay as part or all of the mineral pigmentary material. The term "clay" as used herein and generally in the paper-coating industry refers to china clay or kaolin of which the chief constituent is hydrous aluminum silicate, e. g. kaolinite. It has now been found, that the presence of clay in the hydrophilic planographic printing surface is detrimental to the length of image life in use. And it has been found that by replacing the clay by a non-hydrated or non-hydrous pigment, such as blanc-fixe for example, a coated paper planographic printing plate of considerably longer life can be produced.

Just why clay in the coating of a coated paper planographic printing plate should result in earlier image-failure is not certainly known. It is believed that the

imaging material affixed to the printing surface of a coated paper planographic printing plate adheres largely to the pigmentary portion of the coating. It may be that when clay is in long contact with the aqueous fountain solution the particles thereof tend to swell slightly and so tend to loosen the image; or possibly it may be merely that the clay particles tend to absorb water so strongly that water gradually penetrates between the image and the clay particle to which it is attached and so dislodges the imaging material from the surface.

Whatever the reason may be, the fact remains that non-hydrous pigments retain imaging material longer than clay when used under identical conditions in a coating on a paper planographic printing plate. Of the non-hydrous pigments suitable for use, the preferred ones are titanium dioxide and blanc fixe or precipitated barium sulfate.

The length of life of a plate in use, i. e. the number of prints which can be made therefrom of course, is dependent upon additional factors besides the pigment content of the coating. Important among these factors are the adhesive used to bind the pigment, and the condition of the base to which the coating is applied.

For a paper plate expected to give really long printing runs it is essential that the fibrous base of the plate shall not become saturated with aqueous lithographic solution, with consequent weakening and distortion of the base. A water-impervious barrier-coat interposed between the fibrous base and the planographic printing surface is our preferred means for preventing such saturation and so making possible long printing runs from a paper plate. When such a barrier-coat is used substantially no aqueous liquid reaches the fibrous base and consequently it is not essential for the paper base to have wet-strength properties. Nevertheless, since some penetration of aqueous liquid may be expected through the cut edges of the plate it is preferable to give the paper base some degree of wet-strength, as, for example, by including urea-formaldehyde or melamine-formaldehyde condensate in the paper-making furnish.

Paper coated only on one side is liable to exhibit a tendency to curl. Hence it is preferred in producing coated paper planographic printing plates that the back or non-printing side of the plate also be coated in order to offset to some degree the tendency towards curling which the coating on the printing side may induce. The actual composition of the coating on the back of the plate is of little importance, but it is desirable that the coating be so sufficiently water-resistant that if it inadvertently becomes wetted it will not adhere to the plate cylinder of the printing press or to other objects with which it may come into contact. One suitable coating for the purpose is about 10 pounds per ream of 500 sheets cut 25 x 38 inches, of the evaporation residue of the following composition in parts by weight:

Clay	100
Casein (solvated by ammonia)	18
Dimethylol urea (to insolubilize the casein)	2
Water to make solids content about 40%.	

As a barrier-coat between the paper-base and the hydrophilic coating which provides the planographic printing surface of the plate any convenient coating may be used provided it is both substantially water-impervious and is such that the subsequently applied hydrophilic coating will be anchored securely to it. A very satisfactory coating for the purpose is one deposited from the following composition, given in parts by weight:

Clay	50
A latex of emulsion polymerized styrene and butadiene in the ratio of about 3 to 2	60

A latex of emulsion polymerized polystyrene—mol. wt. 80,000 ---------- 40
Water to make solids content about 40%.

The dry weight of such barrier-coat required per ream of paper will vary considerably, depending upon the surface characteristics of the base stock. It is necessary to apply sufficient so that all fibers are covered. The usual range is from about 4 pounds to about 10 pounds per ream. In any case the coating is adequate if when subjected for 2 minutes to the Cobb absorption test (see Standard Test No. T441 of the Technical Association of the Pulp and Paper Industry) it absorbs not over 0.04 gram of water over an area of 78.5 square centimeters or not over 5.1 grams per square meter. A barrier-coat showing such resistance to water can for our purpose be considered substantially impervious.

The clay in the barrier coat is not detrimental to the life of the printing surface because it is totally enclosed in the latex film and so never is reached or swollen by the aqueous lithographic solution. Its presence in the latex film is advantageous in that it creates some roughness in that film to provide superior anchorage for the hydrophilic coating subsequently applied.

The barrier-coat previously described is oleophilic rather than hydrophilic. Consequently it must be completely covered by the coating which is to provide the planographic printing surface. Otherwise any portions not so covered will pick up ink and so spoil any matter printed therefrom. To ensure complete coverage of the barrier-coat it is expedient to apply the hydrophilic top coating in more than one stage, so that any pin-holes or other imperfections occurring in the first applied hydrophilic layer will be covered up by the later applied coating material.

It is essential that the coating composition used for the top or outmost hydrophilic layer shall contain a water-soluble cellulose derivative as adhesive material. Suitable water-soluble cellulosic adhesives include methyl cellulose, methylethyl cellulose, hydroxyalkyl cellulose such as hydroxyethyl cellulose, the salts of carboxyalkyl hydroxyalkyl cellulose such as sodium carboxymethyl hydroxyethyl cellulose, sodium carboxymethyl cellulose, sodium sulfo-ethyl cellulose, sodium cellulose sulfate, and the like. It has been found, however, that the adhesion of such cellulosic adhesives to the aforesaid barrier-coat may be somewhat deficient in strength and that if coatings containing such cellulosic adhesives are applied directly over such a barrier-coat trouble from cracks in the top or cellulosic coatings is liable to occur. For this reason we prefer to use in the first coating to be applied over the barrier-coat a hydrophilic adhesive which is not a cellulosic adhesive, preferably a protein adhesive, together with a suitable agent to insolubilize said adhesive, such as formaldehyde or a formaldehyde-containing compound.

The originally water-soluble cellulosic adhesive of the top coating must be rendered water-insoluble before the coated sheet can be used as a printing plate. The treatment used to insolubilize the adhesive should not appreciably impair the hydrophilic properties of the adhesive, for the adhesive must not become water-repellent or water-shedding. There are, however, various known treatments for insolubilizing such a hydrophilic cellulosic adhesive without seriously affecting the hydrophilic properties thereof. One insolubilizing treatment that is very effective upon the various cellulose derivative adhesives is carried out by inclusion in the coating compositions of significant quantities of partially condensed amino-resins, such as water-soluble urea-formaldehyde or melamine-formaldehyde condensates, together with sufficient acidic material to keep the pH value of the coating composition below 7. Coatings containing such amino-resin insolubilizers should be force-dried with heat in order to promote "curing" of the resin, and consequential insolubilization of the coating, within a reasonable time. The temperature and/or time required for curing will vary depending upon the particular amino-resin used. Particularly useful amino-resins and the ones we prefer to use are melamine-formaldehyde resins prepared by the partial condensation of one mole of melamine with two to three moles of formaldehyde; for in general such condensates are satisfactorily cured merely by the heating required to dry the water from the coating. One such satisfactory resin is the water-soluble condensate of 1 mole of melamine with 3 moles of formaldehyde.

As has been previously stated, it is essential that neither of the hydrophilic coatings contain clay or other hydrous pigment. Any pigment present in either layer of the hydrophilic coating must be non-hydrous and non-water-swellable. In the first layer the pigment may be either blanc fixe or titanium dioxide, or a mixture of the two. Blanc fixe is cheaper than titanium dioxide and serves just as satisfactorily in the first coating. In the top hydrophilic coating titanium dioxide is preferred.

A preferred first hydrophilic mineral coating to be applied over the previously mentioned barrier-coat is about 10–12 pounds per ream of the evaporation residue of the following coating composition, in parts by weight:

Precipitated barium sulfate (blanc fixe)---------- 100
Casein (solvated by ammonia)---------- 20
Dimethylol urea ---------- 4
Water to make solids content about 35%.

The coating composition used to provide the top or surface coat, however, must contain a water-soluble cellulose derivative and an insolubilizing agent therefor. The said water-soluble cellulose derivative should be present in quantity amounting to from 20 to 70 parts and preferably from 35 to 50 parts by weight for each 100 parts by weight of mineral pigment present. The mineral pigment will contain no clay or other hydrous pigment. From about 2½ to 10 pounds per ream, dry weight, includes the usual range of such coating weights. A typical surface coating would be about 4½ pounds per ream of the evaporation residue of the following coating composition:

	Parts by weight
Titanium dioxide, ball-milled	100
Water-soluble hydroxyethyl cellulose	45
Water-soluble condensate of 1 mole of melamine with 3 moles of formaldehyde	22.3
Wetting agent e. g. the double sulfate of sodium and 7-ethyl-2-methyl undecanol-4	6.0
Foam dispersant e. g. tributyl phosphate	3.0

Acid, e. g. HCl to make pH 5.7.
Water to make solids content about 15%.

The other water-soluble cellulose derivatives mentioned above may be substituted for the hydroxyethyl cellulose of the foregoing example with similar results.

Any of the coating compositions may be applied by conventional coating means, an air-knife coater being very satisfactory.

The paper plate made as hereinbefore described by application of a barrier-coat and two subsequent hydrophilic coats free from clay is, after being dried, subjected to a smoothing or calendering operation to render the surface level. The resulting sheet is then ready to have an image affixed thereto.

The sheet may be coated with a photo-sensitive coating, such for example as bichromated albumin, and dried. It may then be exposed under a negative transparency to actinic light which insolubilizes and renders oleophilic the light-sensitive coating in the areas exposed to the light. The areas under opaque portions of the negative, not being exposed to light, remain soluble and can be washed away leaving the exposed insolubilized areas as an image on the plate. The imaged plate is capable of producing approximately as many copies on an offset duplicator as is a metal plate imaged in the same manner.

The image applied need not be a photo-image, but may be a directly applied image. If desired the plate may be printed with letter-press or other oxidizable ink, and after the ink has dried the plate will print as many copies as will the afore described photo-imaged plate. Or if desired a "Xerox" image (see Journal of the Optical Society of America, vol. 38, No. 12, pages 991–998) may be applied by electrostatically transferring to the plate surface an image of fusible resinous powder which is subsequently heated to fuse the image to the plate surface. Such an imaged plate will print as many copies as the photo-imaged plate previously described.

We claim:

1. Coated paper product suitable for use in preparing a planographic printing plate which comprises a paper base, on one side of said paper base an oleophilic barrier coat substantially impervious to water, over said barrier-coat a first layer of mineral-coating consisting essentially of finely divided non-hydrous mineral pigment and a lesser quantity of insolubilized protein adhesive, and over said first layer of mineral-coating a second layer of mineral-coating consisting essentially of titanium dioxide, cellulose derivative and a cured amino-aldehyde resin, both of said layers of mineral coating being free from hydrous mineral pigment and being insoluble throughout their depths.

2. Coated paper product suitable for use in preparing a planographic printing plate which comprises a paper-base, on one side of said paper base an oleophilic barrier-

coat substantially impervious to water, over said barrier coat a first layer of mineral-coating free from hydrous mineral matter and consisting essentially of insolubilized casein adhesive and precipitated mineral pigment selected from the group consisting of precipitated barium sulfate and titanium dioxide, and over said first layer of mineral coating a hydrophilic layer of mineral-coating consisting essentially of titanium dioxide, cellulose derivative adhesive and a cured amino-aldehyde resin, said hydrophilic layer being free from hydrous mineral pigment and being insoluble throughout its depth.

3. Product of claim 2 in which the cellulose derivative in the hydrophilic top coating is hydroxyethyl cellulose.

4. Coated paper product as defined in claim 1 in which the cellulose derivative is a member of the group consisting of methyl cellulose, methyl ethyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl hydroxyethyl cellulose, sodium sulfo-ethyl cellulose, sodium carboxymethyl cellulose and sodium cellulose sulfate.

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