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PROCESS FOR MAKING PLANOGRAPHIC PRINTING PLATES

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This invention relates to planographic printing plates and to greatly simplified processes for their manufacture. This invention is particularly concerned with novel methods for the development of planographic properties in and on the coatings of coated papers; said coated papers and their surfaces, prior to treatment by certain novel processes, being essentially non-planographic in character and therefore not usable, in a practical sense, as planographic printing plates. Most particularly my invention relates to the manufacture of coated paper planographic printing plates by treating, after it has been coated and dried, an essentially non-planographic coated sheet with an essentially non-aqueous solution containing silicate esters and their reaction products.

By specifying coated paper having a "non-planographic" coating I mean a coating which, when applied to a support-base and dried in conventional equipment, does not exhibit the characteristics common to coated planographic printing plates; the salient above-mentioned "characteristics" are the ability to retain a greasy image, whether applied by lithographic pen, pencil or typewriter, and to retain non-image areas in a clean hydrophilic condition when run on a conventional offset press. By contrast to planographic coated printing plates, non-planographic coated papers soon develop a black tone or scum if attempts are made to use them as plates on conventional offset presses; in other cases non-planographic coated papers may not retain the image hereinbefore described. My invention consists, in part, of methods of imparting planographic properties to non-planographic coatings.

By specifying an "essentially non-aqueous" solution or solutions I mean solutions of organic solvent or solvents having less than 50% by volume of water but preferably having less than 10% of water. One of the objectives of my invention is to take advantage of the superior penetrating powers of solutions of organic solvents containing no water or only a minor amount thereof in the order of 5–25% by volume; such solutions, in contrast with aqueous solutions, penetrate thoroughly and with striking rapidity dried coatings of the type I shall specify.

The use of silicates or silica in planographic printing plate art is by no means novel although there are no previous records which teach the use of organic esters of silica. Thus U.S. Patent No. 2,681,617 teaches the use of a silica aquasol, applied to a planographic surface to form a discontinuous deposit while U.S. Patent No. 2,132,443 discloses that silica, freshly precipitated in a thin film or coating, under certain conditions forms a lithographic surface. In the present invention the silica or silicate compounds which remain in and on the planographic surface behave quite differently and produce results quite different from those disclosed in the before-mentioned patents. In the present invention the application is made only to non-planographic coatings supported on a flexible base; the treatment is not merely that of a surface covering but thoroughly penetrates the coating and often its base support and thus closely resembles a saturation rather than a surface treatment. The saturation feature is a vital part of the present invention for the reason that a mere surface covering, deposit, or film would be removed by erasure or by the abrasion of normal press operations whereas planographic plates made by the present invention may have their surfaces severely abraded and yet will produce legible copy against a clean background thus demonstrating that the treatment has penetrated and the planographic properties have been imparted in depth.

It is a primary objective of the present invention to improve planographic printing plates and, more particularly, to devise manufacturing methods which eliminate many of the operations which are often necessary in conventional processes as practiced up to the present time in the manufacture of commercially-available printing plates.

When paper or other flexible support is coated with planographic or other coatings in order to obtain a planographic surface suitable for conventional offset printing such coatings are nearly always applied from aqueous medium. As a consequence of the use of aqueous coatings it is often necessary to calender or to perform other operations on paper thus coated in order to obtain flatness, reduce curl and so on; furthermore it is often necessary to apply several coats to the side which bears the planographic surface in order to obtain the desired characteristics. With the various operations of coating the back side, coating the front side one or more times, sometimes calendering between coating operations, rewinding after each operation, etc., the manufacturing operation may comprise between five and fifteen separate steps. Through the practice of the art as hereinafter taught it is possible to make excellent planographic plates on a paper or other flexible base and to do so without the many separate steps of manufacture previously necessary. Furthermore, plates made by my methods have desirable properties not previously obtainable by the more involved manufacturing processes.

The attainment of my objectives and subsequent advantages thereof will be readily understood from the following descriptions and examples and the novel features will be more particularly pointed out in the appended claims.

In accordance with my invention it is essential to provide a flexible base or support means which, in addition to being water-resistant and strong, is capable of retaining in a suitably bonded condition a non-planographic coating, examples of which are hereinafter provided. In general terms, I prefer a paper support base; said paper should be well-sized to assure water resistance and may or may not have so-called wet strength. Any flat, dimensionally stable, good quality, strong, well-sized sheet will do. I prefer that the paper weigh between 25 and 80 pounds per 3300 square feet. It will, of course, be obvious that non-planographic coatings such as I shall specify can be applied to other supports such as fabric or lightweight metal.

For the non-planographic coating I prefer one containing as its primary ingredients one or more mineral pigments and between 12 and 35 parts of one or more adhesives per 100 parts of dry pigment. I apply this coating to at least one, but preferably to both sides of the paper or other base by any of the conventional methods such that between 8 and 24 pounds per 3300 square feet of each surface remains after drying; thus if 12 pounds per 3300 square feet of each surface is applied to a 60-pound sheet the resulting weight per 3300 square feet would be 84 pounds.

For the mineral pigment of the above-mentioned non-planographic coating I prefer clays of the type commonly used in the coating and filling of papers. Other pigments or mixtures of pigments which I have used with more or less success include zinc oxide, barium sulfate, titanium dioxide, diatomaceous earth, kaolin, calcium carbonate, silica, silica gel, magnesium carbonate and calcium sulfate. But for reasons of economy and performance I prefer clays as the chief pigment.

For the adhesive I prefer a protein such as casein or soy-bean protein. When, however, protein is the sole

adhesive, plates having inferior performance may result, which is to say that the image may not be adequately retained or the coating may crack when folded; in consequence, I generally prefer to use, along with the protein, a more flexible adhesive such as a synthetic latex containing polyvinyl chloride or polyvinyl acetate or a polyester resin, or a styrene-butadiene copolymer, or an alkyd resin or other high polymers which impart sufficient strength and flexibility. Other ingredients may be added to impart plasticity, reduce foaming or viscosity of the wet coating mixture or to impart other desirable properties so long as there is no interference with planographic properties when plates are, eventually, made.

It will be obvious to those skilled in the art that my process can be extended to numerous non-planographic coatings wherein the adhesive, such as starch and starch derivatives, is other than those specifically listed above.

As specific examples of the non-planographic coatings which I have applied to a flexible base and, later, have treated to impart planographic properties with more or less success I give the following:

[Parts by weight (dry)]

	Clay	Casein	Synthetic Latex
Example 1	100	28	4
Example 2	100	24	8
Example 3	100	24	0
Example 4	100	21	3
Example 5	100	18	6
Example 6	100	15	3
Example 7	100	18	3
Example 8	100	12	3
Example 9	100	18	0
Example 10	100	15	0

In preparation of coatings 1 through 10 I have achieved excellent success by using, as the synthetic latex, materials such as styrene-butadiene copolymers of which the product known as 512–R manufactured by the Dow Chemical Co. of Midland, Michigan, is an example. As previously indicated, other materials having suitable flexibility and compatibility will work as well.

The coatings indicated in Examples 1 through 10 were prepared with ammoniated water; the dry ingredients comprised 35 to 40% of the total weight. These aqueous coatings were then applied to a flexible paper base of the type previously described, dried in a conventional drying oven and calendered to produce a smooth, flat but not glossy surface. In some cases coatings having as much as 65% dry ingredients were prepared and successfully applied. Coatings were applied by conventional methods and machinery. In nearly all cases coatings were applied simultaneously or singly to both sides of the paper base in order to reduce curl. In some cases the surface of the dried coating was buffed or otherwise treated to produce a dull or matte finish. Coated papers prepared in the indicated manner were then ready, without further preparation or treatment, for the application of the solution or solutions having the power to impart planographic properties.

For my planographic solution or solutions I use a solution containing less than 50% by volume of water and preferably a solution containing less than 10% by volume of water in order to avoid wrinkling, cockling, and other difficulties which seemingly always accompany the application to paper of aqueous solutions or coatings. The non-aqueous solvents in this solution may include acetone, diethyl ketone, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, benzene, petroleum ether, methyl alcohol, ethyl alcohol, isopropyl alcohol, glycerine, ethylene glycol, polyethylene glycol, ethyl acetate, ethyl proprionate, butyl acetate, dibutyl ether and other similar liquids—all have been used with more or less success. However, for reasons of economy and simplicity I prefer to use, whenever possible, only such commonly-used solvents as methyl and ethyl alcohol, acetone and dimethyl ketone; generally a mixture of an alcohol and a ketone plus the active ingredients of the solution are all that is required for excellent results.

The active ingredients of my planographic solution are silicate esters and/or their hydrolysis products and may include the compounds resulting from the reaction of these silicate esters and their hydrolysis products with hydroxides of ammonia, barium, sodium or other alkaline materials. Among other things these silicate esters are characterized by their solubility in organic solvents and their insolubility or slight solubility in water. Examples of these esters are tetraethyl orthosilicate; condensed ethyl silicate and ethyl silicate 40 as manufactured and sold by Carbide & Carbon Chemicals Co. of New York City. These silicate esters are liquids having solvent and penetrating properties and, for the most part, distill below 200° C. at 760 mm. pressure; calculated as SiO_2 their silica contents range between 25 and 55% by weight with the content generally falling between 28.0 and 40.0%.

It will be clear to those skilled in the art that silicate esters other than those specifically listed may be used in practicing the art to be here taught but, without being limited thereto, I prefer generally to use condensed ethyl silicate for the preparation of my planographic solutions.

In preparing my planographic solutions and in their ultimate application to the non-planographic coated paper I can follow any one of several procedures and still obtain substantially the same end-result as will now be shown. In one case, for example, it is possible to react partially the ethyl silicate with water, apply it to the coated base, remove the excess and then to complete the essential chemical reactions by applying, before drying can occur, a second solution containing alkaline agents such as ammonium or barium hydroxide; following this second bath the excess solution is again removed and the paper thus treated is dried; on cutting into suitable sizes, paper thus treated may be used on a conventional offset press as a printing plate. Alternatively I may substitute an ammonia vapor or other alkaline vapor treatment for the second bath; this procedure avoids the problem of contamination of the second bath by the first. As a further modification I may combine the first and second baths, filtering if necessary to remove any undesirable precipitate; the resulting solution or the supernatant liquid, in cases where filtration is necessary, may then be applied to the non-planographic coated base which, after drying and cutting to size, can be used with excellent success as a planographic printing plate on a conventional offset printing press. In applying any of the solutions described in the foregoing I prefer to obtain complete saturation of the coating and its supporting base but I have found that it is also possible to make a satisfactory product even though complete saturation may not be achieved; thus I may apply my solutions by a rapid passage or dip of the coated base or I may apply the solutions to only one side of the coated base as by a rotogravure roll, squeeze rolls, or similar means and, thus, impart planographic properties to only one side of the hitherto nonplanographic coated base. The only requirement of the method of application appears to be that no excess of solution prior to drying or solid ingredients after drying shall be left on the surface of the coated base thus treated; such excesses result in loose residues which, unless removed, contribute to poor images and to toning or scumming of the non-image areas.

Following are examples of essentially non-aqueous solutions used in practicing my invention by the two-bath or two-solution process as hereinbefore described.

Silicate-Containing Solutions

[Parts by volume]

	Condensed Ethyl Silicate	95% Ethanol	Methyl Ethyl Ketone	Water	Conc. Acid
Example 11	129	100	200	30	2
Example 12	170	100	200	40	2
Example 13	90	100	200	21	2
Example 14	60	100	200	21	2
Example 15	100	100	200	25	2
Example 16	100	100	200	80	2

Examples 17–22: Identical with Examples 11–16 except that to each hundred parts by weight of solution is added between 5 and 15 parts by weight of a humectant chemical; glycerine, polyethylene glycol of molecular weight 500 to 2000, and ethylene glycol are all satisfactory.

In Examples 11–22 concentrated hydrochloric acid is used. Equally satisfactory results are obtained with sulfuric acid or trichloroacetic acid.

In preparing the solutions of Examples 11–22 all ingredients except the acid are mixed together, than the acid is added and the solution is agitated for twenty minutes after which it is ready to apply according to the methods previously described.

The solutions of Examples 11–22 are the "first" or silicate-containing solutions. Examples of the "second" or alkaline solutions now follow.

Alkaline Solutions

	Alkaline Agent	Solvent Mixture	Alkaline Agent Parts by Weight
Example 23	$Ba(OH)_2$	acetone-methanol 1:1	2
Example 24	$Ba(OH)_2$	methyl ethyl ketone-methanol 1:1.	2
Example 25	NaOH	do	2
Example 26	$Ba(OH)_2$	do	1
Example 27	$Ba(OH)_2$	do	½
Example 28	$Ba(OH)_2$	methyl ethyl ketone-methanol 1½:1	2
Example 29	NH_4OH (28%)	do	2
Example 30	NHOH (28%)	do	6

Any one of the alkaline solutions of Examples 23–28 may be used to follow any one of the solutions of Examples 11–22 on bases bearing any one of the coatings of Examples 1–10 although in practical operations it will be found that, depending on coating method, coating weight, porosity, formulation and other factors the combination of solutions which gives the best results may vary considerably from one coated base to the next.

It is of significance to note that if the acid is omitted from the first bath the application of the second bath will not result in the full development of planographic properties whereas complete development of planographic properties takes place in a matter of seconds when the first solution is prepared according to one of the Examples 11–22; this fact is taken as indicating that in the first bath the hydrolysis is only partial and is completed in situ by the application of the second bath. Furthermore, planographic properties are only slightly developed or are not developed at all if, between baths, the coating and its surface are completely dried; this is true even though the coating may again be treated with a water-containing but non-silicate-containing solution prior to application of the second bath. Thus it is clear the two-bath process does not merely consist of applying ordinary inorganic silicates dissolved or suspended in a largely organic solution.

In practicing my invention by the foregoing two-bath

or two-solution process one finds that, since the second bath sooner or later becomes contaminated by liquid residues entering along with the still-undried coated paper which has just passed through the first bath, it is necessary to filter the second bath continuously in order to remove extraneous matter. In practical operations the necessary equipment may not be available. In consequence in the first modification of my process the second bath is eliminated and instead the coated base, having no surface excess but still bearing in liquid form a portion of the first bath as given in Examples 11–22, is passed briefly through a chamber containing volatile amines or ammoniacal vapor after which the paper thus treated is thoroughly dried. I have found that this vapor treatment is most efficacious and allows for highest running speeds if the temperature in the chamber is maintained at least as high as 100° F. but no higher than 200° F. Agitation of the vapors of the chamber is very beneficial and allows rapid completion of the neutralization reactions, however care must be taken to avoid prolonged exposure inasmuch as any softening of the coating or substantial effect on the base-support itself would necessitate later calendering and would thus defeat the essential purpose of the process—which is its simplicity. It is a vital and important part of this invention that no obvious softening or plasticization of the coating occurs in the rather fleeting exposure to solutions or vapors.

As a further modification and simplification of the process I combine the first bath with the second bath and treat a non-planographic coated base with this combined bath and thereby impart planographic properties equivalent in all essential respects to those obtained by the two-bath process or by the one-bath-plus-vapor-chamber process hereinbefore described. Furthermore I find that it is possible to proceed thus with flexible bases bearing any of the non-planographic coatings of Examples 1–10 and with any combination of the silicate solutions of Examples 11–22 with any of the alkaline solutions of Examples 23–28 noting, however, that certain combinations sometimes give better results, in terms of planographic plate performance, than others depending on the porosity of the coating, weight of coating, formulation, method of application, and so on. Depending on the solvents and the alkaline agent it may sometimes be necessary to filter the alkaline solutions, which result when the silicate solution is combined with the alkaline solution, in order to remove objectionable residues which may otherwise be present and which would produce inferior planographic properties. In order to eliminate the need for filtration and in order to simplify further the preparation of this bath it is possible to prepare the bath, without the use of an acid, by merely adding the indicated amount of ammonium hydroxide or an equivalent amount of triethanol amine directly to the solvent solution containing the required amount of silicate ester; in such situations there is no need for the addition of extra water inasmuch as sufficient is present in the 28% ammonium hydroxide; furthermore, the acids used in the two-bath procedure may also be omitted. Solutions prepared by the direct addition of a solution of alkaline materials without the prior addition of acids may require a somewhat longer period for hydrolysis before being ready for use but are nevertheless entirely satisfactory for imparting planographic properties to otherwise non-planographic coatings. While bases such as sodium hydroxide and barium hydroxide may be substituted for ammonium hydroxide or triethanolamine or other liquid base the solution then requires filtration prior to use in order to remove objectionable residues.

As specific examples of plates which have been made by my process and its modifications as hereinbefore described and to provide specific indication of the results

and performance which can be thus obtained I give the following:

TWO-BATH PROCEDURE

	Coating as in Example No.	First Bath as in Example No.	Second Bath as in Example No.
Example 31	3	11	28
Example 32	4	11	28
Example 33	5	11	28
Example 34	5	11	29
Example 35	5	11 plus 10 parts polyethylene glycol 1000 per 100 of solution.	28
Example 36	5	11	30

ONE-BATH PLUS VAPOR-CHAMBER PROCEDURE

Example 37	5	11	none.
Example 38	5	11 plus 10 parts polyethylene glycol 1000 per 100 of solution.	none.

ONE-BATH PROCEDURE

Example 39	3	baths 11 and 28 combined; pH above 8.
Example 40	4	Do.
Example 41	5	Do.
Example 42	5	baths 11 and 30 combined; pH above 8.
Example 43	5	bath 11 lacking only acid; 10% NH_4OH (28%) directly added; pH above 8.

The base used in preparing the plates of Examples 31–43 was a smooth, strong, calendered, water-resistant paper such as described earlier in this specification; it carried approximately 15 pounds of non-planographic coating per 3300 square feet of surface. After calendering it was treated in accordance with the procedures previously described and in accordance with the specific steps of Examples 31–43; the treatment imparted scarcely one-half pound of additional weight per 3300 square feet of surface.

In making press runs with these plates on a conventional offset press using conventional inks and solutions the following results were noted:

Plates from Example No.	Performance
31	200 excellent copies; then began to lose image.
32	300 excellent copies; then began to lose image.
33	1,500 excellent copies; no loss of image.
34	1,000 excellent copies; slight loss of image.
35	500 excellent copies; surface somewhat greasy.
36	1,000 excellent copies; slight loss of image.
37	1,000 excellent copies; no loss of image.
38	1,000 excellent copies; surface somewhat greasy.
39	200 copies; not sufficiently hydrophilic.
40	Do.
41	Do.
42	1,500 excellent copies; no loss of image.
43	Do.

From the foregoing results it is clear that a soluble liquid base may yield superior results whenever the one-bath process is used. It appears clear that the barium hydroxide, which is quite satisfactory for a two-bath system, precipitates too much of the silicate and therefore the ability to impart planographic properties is impaired.

In the Examples 31–43 it is noted that no calendering or other treatment, following the application of the planographic solutions, is necessary in order to obtain satisfactory plates. Furthermore, it is noted that the plates run well in every respect and exhibit a striking ability to develop rapidly the printed image while at the same time maintaining non-imaged areas free from scumming and background tone due to adherent ink. Furthermore, it is noted that planographic printing qualities are imparted not only to the surface but also in depth and are in no sense a mere surface treatment; the presence of treatment in depth is evidenced by these plates' ability to withstand abrasive wear and, after thus having a portion of the surface removed, to retain a newly-imparted image while at the same time retaining the non-imaged areas of the abraded portion in a clean and hydrophilic condition. It is further noted that the non-planographic coated papers used as bases in these examples do not, when run as planographic plates on a conventional press, perform satisfactorily but develop deep tone overall after perhaps 25 revolutions of the press and no amount of press adjustment can compensate for the absence of the essential planographic qualities. It is further noted that efforts to produce essentially the same end-results through the use of essentially non-aqueous solutions of silicic acid sodium silicate or ammonium silicate prepared by dissolving or attempting to dissolve said compounds in various solvents and solvent mixtures have proved, in all cases, fruitless. It is further noted that aqueous solutions or dispersions containing such compounds as silicic acid, sodium silicate, ammonium silicate, silica or barium silicate invariably cause cockling or wrinkling of the sheet and usually softening of the coating too, whereas these disadvantages rarely, if ever, are found in the practice of my invention according to the examples listed. It is further noted that the use of these aqueous dispersions or solutions when applied to the coated sheet, for an exposure period twice as long as commonly used in the application of my essentially non-aqueous solutions, fails to impart planographic properties to any substantial depth of the coating. It is further noted that in order to obtain planographic properties of any consequence through the application of these aqueous solutions, dispersions, or aquasols it is necessary to apply on a dry basis at least 2 to 3 pounds of silica or silicates per 3300 square feet of surface whereas in the practice of my invention the added weight is never more than 1.5 pounds per 3300 square feet of surface and more commonly is less than 1.0 pound per 3300 square feet of surface.

In extending and broading still further the possible application of my invention I have also applied the art taught in Examples 11–43 to coated surfaces already having planographic properties. Thus, I have treated in accordance with Examples 11–43, paper planographic plates such as are commercially available in the open market and have found some enhancement of planographic properties. Thus it will be obvious to those skilled in the art that the manufacture of existing planographic plates can be simplified and the product improved by utilizing my essential discovery in treating coated surfaces already possessed of planographic properties.

What I claim as new is:

1. The process of making a planographic plate comprising treating a flexible paper base having a non-planographic coating with an acidified solution of a lower alkyl silicate ester in a solvent having less than 50% by volume of water, and then treating said coated base with an alkaline solution in an organic solvent, thereby providing a planographic surface on said base.

2. The process of making a planographic plate comprising coating a flexible base sufficiently smooth for planographic printing with a non-planographic layer, depositing a lower alkyl silicate ester on and in said layer from an essentially organic solution containing less than 50% by volume of water, and exposing the deposited layer to alkaline vapors, thereby providing a planographic coating on said base.

3. The process of making a planographic plate comprising coating a flexible paper base with a non-planographic layer comprised essentially of a mineral pigment and adhesives selected from the class consisting of protein and resinous adhesives, depositing particles of partially hydrolyzed ethyl silicate on and in said layer from an essentially organic solution containing less than 50% by volume of water, and exposing the deposited layer to

alkaline vapors to complete the hydrolysis of the ethyl silicate.

4. The process of making a planographic plate which comprises applying to a coated flexible paper base a composition formed by dissolving a lower alkyl silicate in an essentially organic solvent containing water in an amount less than 50 percent by volume and adding thereto an alkaline agent in an amount effective to hydrolyze said silicate, and drying said base thereby providing a planographic coating thereon.

5. The process defined by claim 4 wherein the paper base is coated with a composition comprising mineral pigment and adhesive.

6. The process of making a planographic plate which comprises applying to a flexible paper base having a coating comprising mineral pigment and adhesive, a composition formed by dissolving ethyl silicate in an essentially organic solvent containing water in an amount less than 50 percent by volume and adding thereto an alkaline agent in an amount effective to hydrolyze said silicate, and drying said base thereby providing a planographic coating thereon.

7. The process of making a planographic plate which comprises applying to a coated flexible paper base a solution of a lower alkyl silicate in an essentially organic solvent containing less than 50 percent by volume of water and an alkaline agent effective to hydrolyze said silicate, and drying said base, thereby providing a planographic coating thereon.

8. The process defined by claim 7 wherein the solution and alkaline agent are first combined and then applied to the base.

9. The process of making a planographic plate which comprises applying to a coated flexible paper base a solution of ethyl silicate in an essentially organic solvent containing less than 50 percent by volume of water and an alkaline agent effective to hydrolyze said silicate, and drying said base, thereby providing a planographic coating thereon.

10. The process of making a planographic plate which comprises applying to a coated flexible paper base an acidified solution of a lower alkyl silicate in an essentially organic solvent containing less than 50 percent by volume of water and an alkaline agent effective to hydrolyze said silicate, and drying said base, thereby providing a planographic coating thereon.

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