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**METHOD FOR IMAGING PLANOGRAPHIC PLATE**  
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This invention relates to the art of planographic printing and it relates more particularly to the art of lithographic printing and to the method for the preparation of an imaged master for use in the practice of same.

The master may be in the form of a paper base master or alternatively may comprise such material bonded to a substrate of e.g. plastic, metal or textile fabric, the master as a whole having sufficient flexibility for bending about a typewriter platen but with sufficient strength to maintain dimensional stability for at least the number of copies that it is desired to produce therefrom.

In the art of planographic printing using paper base masters the normal procedure is first to render the surface of the master lithographic, then apply an oleophilic image to the paper master and finally apply a so-called etch composition to the imaged master so that the non-imaged areas become hydrophilic whilst leaving the imaged areas oleophilic. The treated master can then be used in an off-set planographic printing machine provided with ink and water fountains so that a reproduced image is transferred only from the imaged areas onto the offset roller and thence onto the paper to be printed. The paper base master used in such a procedure frequently consists of a wet-strength paper coated with a series of coatings to obtain a lithographic surface, i.e. one having a critical balance between oleophilic and hydrophilic properties. Thus, if the surface is too oleophilic, ink will not be attracted preferentially to the imaged areas but will in addition be picked up by non-image areas giving the phenomena of "speaking" and "scumming." If, on the other hand, the surface is too hydrophilic, the ink will be repelled from the imaged areas and the greasy image will be unstable i.e. will tend to disappear from the surface of the master during use. Consequently considerable care is necessary in the selection of materials for and in preparation of the master in order to obtain the aforesaid critical balance. For example, in one method of preparing paper masters, paper having a resin added to the pulp during the paper-making operation to confer so-called wet strength is first coated with a slurry of casein, clay and zinc oxide to provide an oil-receptive barrier coat, the barrier coat is coated with a slurry of clay and casein and this second coating is treated with a so-called wash coat comprising an aqueous solution of a polyvalent metal salt which confers lithographic properties on the clay-casein coat. The resultant master is brushed to a smooth finish and, provided due care has been exercised in the choice of materials and preparation of the master, possesses to a greater or lesser degree the aforesaid critical balance. The master may then be imaged, treated with a so-called etch solution (frequently comprising a buffered solution of phosphoric acid). Masters produced by this procedure are relatively expensive to produce and depend for their performance on having achieved the critical balance between oleophilic and hydrophilic properties.

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It is an object of this invention to produce and to provide a method for producing an inexpensive lithographic master which is simple in construction, which is easy in operation, which is less critical from the standpoint of balance between oleophilic and hydrophilic properties, which is capable of use to produce a fairly large number of copies of good quality, and which is capable of good image retention without specking or picking and it is a related object to provide a new and improved method for imaging same.

In accordance with the practice of this invention, use can be made of paper masters prepared from paper not having a critical balance of hydrophilic and oleophilic properties but which is, in fact, distinctly oleophilic. Paper of this type is normally prepared by applying a slurry of a hydrophilic colloid binder e.g. casein, containing a filler and/or pigment, e.g. clay and/or zinc oxide to paper and calendering the coated paper. Such paper is produced in large quantities and can be produced inexpensively as compared with conventional paper masters.

Thus it has been found that it is possible to reproduce copies planographically from imaged masters prepared from paper of the art paper type, particularly if the paper has a high pick resistance, if the imaged master is subjected to a specific etch treatment prior to printing.

According to the invention, therefore, there is provided a method of preparing an imaged paper base master for use in a planographic printing process which comprises imaging the surface of a paper base, said surface being non-lithographic and oleophilic and which preferably has a high pick resistance, and subjecting the imaged surface to the action of a pre-etch solution comprising an aqueous solution of a polyvalent metal salt, preferably also containing a hydrophilic colloid, and then subjecting the imaged surface to the action of an aqueous, preferably mildly acidic, etch solution containing an anion which reacts with the metal cation in the pre-etch solution to form an insoluble or sparingly soluble precipitate.

By the term "non-lithographic" as applied to the paper surface is meant that an imaged surface of this nature is incapable of being directly used in a planographic printing process when subjected to the action of an aqueous phosphoric acid etch solution.

By the term "high pick resistance" is meant a pick resistance of at least 7A and preferably at least 9A when determined on the dry surface of the master according to the standard Dennison wax test.

The surface of the master should also preferably have high-surface strength in the moist state. This may be achieved by the presence of resins in the paper to confer wet-strength.

Papers with a pick resistance of less than 7A and poor moist strength are capable of producing a limited number of copies when used as masters according to the invention. However, from a practical view-point, papers of high pick resistance capable of consistently printing 25 to 300 or more copies are preferred.

The pre-etch solution may be an aqueous solution of any convenient polyvalent metal salt provided that this is not deleterious to any extent to the paper base or to the greasy image. For example, one should not use salts which are strong oxidizing agents. The metal may be divalent or trivalent or may even possess a higher valency. In general, the amount of salt required will depend on the extent to which the paper is oleophilic i.e. the more

oleophilic the paper the greater will be the quantity of salt required. The latter requirement will of course depend on the solubility of the salt in the pre-etch. The choice of salt will depend on questions such as its solubility, its efficacy and its cost. One may, for example, use salts of zinc, nickel, calcium, copper, cobalt, iron, lead, magnesium, cadmium, barium, manganese and aluminum. The salt may be derived from a mono- or poly-basic acid and the acid may be organic or inorganic. Depending upon the nature of the metal ion, suitable acids include acetic acid, hydrochloric acid, nitric acid and sulphuric acid. In general, zinc salts are satisfactory and relatively inexpensive and it is found to be advantageous to use zinc acetate.

In order to ensure a combination of good pick resistance with rapid pick-up of image from the inked master it is desirable to include in the pre-etch solution a hydrophilic colloid. The hydrophilic colloid should be of such a nature and be used in such a manner that the viscosity of the pre-etch is kept sufficiently low to permit easy application to the surface of the master by the customary manual or automatic applicators. The hydrophilic colloid may be natural or synthetic or may be a derivative of a natural substance. Colloids which may be used include cellulose derivatives, e.g. methyl cellulose, hydroxypropyl methyl cellulose and carboxymethyl cellulose, gum tragacanth, guar gum, gum arabic, gelatine and polyvinyl alcohol. It is particularly preferred to use gum tragacanth since this colloid gives rise to aqueous solutions compatible with most metal salts and of a convenient viscosity.

The hydrophilic colloid should also not be one which reacts with the metal salt to form a precipitate although it need not necessarily be non-reactive.

The pre-etch solution may also contain an inert colloidal solid material in order to improve the running properties of the master and to reduce sensitivity towards handling. The colloidal material may be, for example, silica and this is conveniently added in the form of a silica aquasol.

Subject to the general considerations described above the pre-etch solution may contain 2-30%, preferably 8-15%, by weight of salt, and, if present, 0.2-5%, preferably 0.5-2%, by weight of hydrophilic colloid and 0.5-5% by weight of inert colloidal solid material.

The pre-etch solution may also contain a compatible surface agent to improve wetting of the paper base master. Suitable surface-active agents include, for example, non-ionic wetting agents e.g. condensation products of ethylene oxide with alkyl phenols, or low molecular weight alcohols e.g. methanol, ethanol, propanol or butanol.

To prepare the pre-etch solution, the metal salt and hydrophilic colloid are separately dissolved in water and the two solutions mixed. For example, the hydrophilic colloid may be dissolved in water at 70-80° C. as a 5%

solution. This may then be stirred at 70-80° C. until the colloid forms a uniform colloidal solution, cooled to about 30° C. and then added to the metal salt solution at 25-30° C. Any further ingredient may then be added and the mixture stirred until it is thoroughly homogenized.

The etch solution may be any conventional solution of this type provided that it contains no ingredients which are detrimental to the paper and is capable of reacting with the pre-etch solution as defined above. Solutions of this type are usually buffered to an intermediate acid pH, for example, in the case of a phosphoric acid etch solution using sodium dihydrogen phosphate, which may or may not but preferably does contain a humectant, e.g. glycerol or other polyhydric alcohol, to prevent the surface drying out too quickly and one or more substances to facilitate wetting of the paper e.g. lower alkanols and/or compatible wetting agents. It is preferred to use an etch solution based on phosphoric acid and/or phosphates, since this is the most frequent type used in lithographic printing. It is possible, however, to substitute an etch solution based on an acid, such as oxalic acid, chromic acid, silicic acid, or water-soluble salts thereof, or a water-soluble salt capable of forming an insoluble or sparingly soluble precipitate with the metal of the pre-etch solution, e.g. the following combinations of cations (in the pre-etch) and anions (in the etch) are suitable:  $\text{Ca}^{++}-\text{C}_2\text{O}_4^{--}$ ,  $\text{Ba}^{++}-\text{SO}_4^{--}$ ,  $\text{Pb}^{++}-\text{CrO}_4^{--}$ ,  $\text{Zn}_2^{++}$  or  $\text{Cu}_2^{++}-\text{Fe}(\text{CN})_6^{--}$ .

After the imaged master has been subjected to the action of the pre-etch and etch solutions it is attached to the cylinder of an off-set duplicator provided with ink and water fountains and copies are taken in the usual manner.

An inherent advantage of the process according to the invention is that it can be used to reproduce images from imaged paper having the characteristics set forth above i.e. it can be used to make copies of pages in periodicals and books. A further advantage of the process according to the invention is that the paper surface prior to imaging is capable of receiving a stronger image, due to its inherent oleophilic characteristics, than paper surfaces which are lithographic.

In order that the invention may be well understood the following examples are given by way of illustration only. In the examples parts and percentages are by weight.

A series of pre-etch solutions were prepared from various metal salts and hydrophilic colloids. The hydrophilic colloid was first dissolved in water at 70-80° C. as a 5% by weight solution. This was stirred at 70-80° C. until the colloid had formed a uniform colloidal solution cooled to about 30° C. and then added to an aqueous solution of the metal salt. Further ingredients, in some cases, were added and the mixture stirred until thoroughly homogenized.

Table I.—Composition of pre-etch solutions

Pre-etch solution No.	Formula of metal salt	Name of hydrophilic colloid	Composition of pre-etch (percent by weight)			
			Metal salt	Hydrophilic colloid	Water	Other ingredients
(1)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Guar gum-----	10.0	1.0	89.0	(Glycerol 36.7).
(2)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Gum arabic-----	10.0	1.0	89.0	
(3)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Methyl ethyl cellulose-----	10.0	1.0	89.0	
(4)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Hydroxypropyl methyl cellulose-----	10.0	1.0	89.0	
(5)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Gum tragacanth-----	10.0	1.0	89.0	
(6)-----	$\text{Zn}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	Hydroxypropyl methyl cellulose-----	6.7	0.7	44.1	
(7)-----	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	Gum tragacanth-----	10.0	1.0	89.0	
(8)-----	$\text{CaCl}_2$ -----	do-----	10.0	1.0	89.0	
(9)-----	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(10)-----	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(11)-----	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(12)-----	$\text{Pb}(\text{C}_2\text{H}_3\text{O})_2 \cdot 3\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(13)-----	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(14)-----	$\text{Cd}(\text{C}_2\text{H}_3\text{O})_2 \cdot 2\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(15)-----	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	
(16)-----	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ -----	do-----	10.0	1.0	89.0	

Table I.—Composition of pre-etch solutions—Continued

Pre-etch solution No.	Formula of metal salt	Name of hydrophilic colloid	Composition of pre-etch (percent by weight)			
			Metal salt	Hydrophilic colloid	Water	Other ingredients
(17)-----	FeCl <sub>3</sub> ·6H <sub>2</sub> O-----	Gum tragacanth-----	10.0	1.0	89.0	
(18)-----	MnSO <sub>4</sub> ·4H <sub>2</sub> O-----	do-----	10.0	1.0	89.0	
(19)-----	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O-----	do-----	10.0	1.0	89.0	
(20)-----	{FeSO <sub>4</sub> ·7H <sub>2</sub> O-----	{do-----	{5.0	{1.0	{89.0	
(21)-----	{MgSO <sub>4</sub> ·7H <sub>2</sub> O-----	{do-----	{5.0	{1.0	{89.0	
(22)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	Polyvinyl alcohol-----	10.0	1.0	89.0	
(23)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	Gelatine-----	10.0	1.0	89.0	
(24)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	Gum tragacanth-----	13.3	0.7	86.0	
(25)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	8.1	0.9	89.9	(0.13 Lissapol N). <sup>1</sup>
(26)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	20.0	1.0	79.0	
(27)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	26.7	0.7	72.6	
(28)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	5.0	0.5	94.5	
(29)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	5.0	1.0	94.0	
(30)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	13.3	1.0	85.7	
(31)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	10.0	0.5	65.0	(25.0 Syton W-20). <sup>2</sup>
(32)-----	Zn(C <sub>2</sub> H <sub>3</sub> O) <sub>2</sub> ·2H <sub>2</sub> O-----	do-----	12.40	0.53	75.47	(11.60 Syton W-20).
			6.20	0.26	87.74	(5.80 Syton W-20).

<sup>1</sup> Lissapol N is non-ionic surface active agent derived from ethylene oxide and an alkyl phenol sold by Imperial Chemical Industries Ltd.

<sup>2</sup> Syton W-20 is a silica aquasol (solids content 15%) sold by Monsanto Chemicals Ltd.

A corresponding number of paper masters of art paper each having a pick resistance of 12A were then imaged with carbon and cotton lithographic typewriter ribbons. Each imaged surface was rubbed with one of the pre-etch solutions and then with a commercial phosphoric acid etch solution having a pH of 5.6–5.8 whilst the pre-etch solution was still wet on the paper. The masters were then attached in turn to the cylinder of a commercial off-set duplicator provided with ink and water fountains. The results obtained are given in Table 2.

Table 2.—Results of trial duplicator runs

Pre-etch solution code No.	Number of Copies Run	Number of copy at which picking first occurred
(1) (a)-----	88	75
(1) (b)-----	100	75
(2) (a)-----	125	100
(2) (b)-----	175	150
(3) (a)-----	160	130
(3) (b)-----	175	150
(4) (a)-----	232	225
(4) (b)-----	225	200
(5) (a)-----	258	225
(5) (b)-----	250	225
(5) (c)-----	140	125
(6)-----	160	125
(7)-----	117	100
(8)-----	175	150
(9)-----	225	200
(10)-----	100	100
(11)-----	218	200
(12)-----	225	200
(13)-----	125	112
(14)-----	175	150
(15)-----	125	125
(16)-----	167	125
(17)-----	175	125
(18)-----	150	125
(19)-----	200	150
(20)-----	175	125
(21)-----	196	175
(22)-----	225	200
(23) (a)-----	216	200
(23) (b)-----	137	125
(23) (c)-----	125	120
(24)-----	100	75
(25) (a)-----	53	>53
(25) (b)-----	100	75
(26)-----	50	>60
(27)-----	80	>60
(28)-----	75	>75
(29)-----	100	100
(30)-----	125	>125
(31) (a)-----	175	150
(31) (b)-----	175	125
(31) (c)-----	250	>250
(31) (d)-----	100	>100
(31) (e)-----	125	>125
(32)-----	150	150

These experiments were repeated using paper masters having various pick resistance values and using pre-etch solutions No. 31. The results obtained are shown in Table 3.

Table 3

Paper master No.	Pick resistance value	Number of copies run	Number of copy at which picking first occurred
1-----	9A-----	{(a) 150-----	125
		{(b) 125-----	100
2-----	8A-----	{(a) 100-----	>100
		{(b) 117-----	100
3-----	6A-----	{(a) 75-----	50
		{(b) 100-----	75
4-----	7A-----	50-----	50
5-----	8A-----	140-----	125
6-----	8A-----	100-----	75
7-----	7A-----	100-----	>100
8-----	8A-----	200-----	175

It will be apparent from the foregoing that there is provided an inexpensive and readily available lithographic master which is adapted to a new concept for the development of the oleophilic, ink receptive, water repellent imaged portion and the hydrophilic, water receptive ink repellent non-imaged portion of the plate.

It will be understood that changes may be made in the details of construction, arrangement and operation without departing from the spirit of the invention especially as defined in the following claims.

I claim:

1. In the method of preparing an imaged lithographic plate on a base sheet having a non-lithographic surface and having a pick resistance of at least 7A, comprising the steps consisting of imaging the surface of the sheet with an ink receptive, water repellent, oleophilic material, treating the imaged surface of the sheet with a pre-etch solution of a salt of a polyvalent metal, and thereafter treating the surface with an acidic etch solution containing an anion which reacts with the metal cation of the pre-etch to form a relatively insoluble precipitate.

2. The method as claimed in claim 1 in which the polyvalent metal salt is present in an amount within the range of 2 to 30% by weight of the solution.

3. The method as claimed in claim 1 in which the polyvalent metal salt is present in an amount within the range of 8 to 15% by weight of the solution.

4. The method as claimed in claim 1 which includes a hydrophilic colloid present in the pre-etch solution in an amount within the range of 0.2 to 5% by weight.

5. The method as claimed in claim 4 in which the hydrophilic colloid is dissolved in the pre-etch solution in an amount within the range of 0.5 to 2% by weight.

6. The method as claimed in claim 1 in which the metal cation of the pre-etch solution is selected from the group consisting of zinc, nickel, calcium, copper, cobalt,

iron, lead, magnesium, cadmium, barium, manganese and aluminum.

7. The method as claimed in claim 4 in which the hydrophilic colloid is selected from the group consisting of methyl ethyl cellulose, hydroxypropyl methyl cellulose, carboxymethyl cellulose, gum tragacanth, guar gum, gelatin and polyvinyl alcohol.

8. The method as claimed in claim 1 which includes an inert colloidal solids in suspension in the pre-etch solution present in an amount within the range of 0.5 to 5% by weight.

9. The method as claimed in claim 8 in which the inert colloidal solids suspended in the pre-etch solution comprise silica.

10. The method as claimed in claim 8 which includes a surface active agent in the form of a non-ionic wetting agent.

11. The method as claimed in claim 1 in which the anion of the acidic etch solution is selected from the group consisting of phosphoric acid, oxalic acid, sulphuric acid, chromic acid, silicic acid, acid ferrocyanide and salts thereof.

12. The method as claimed in claim 1 in which the acidic etch solution contains a humectant.

13. The method as claimed in claim 12 in which the humectant is a polyhydric alcohol.

14. In the method of preparing an imaged lithographic plate on a base sheet having a non-lithographic surface, and a pick resistance of at least 7A, the steps consisting

of imaging the surface with an ink receptive, water repellent imaging material, treating the oleophilic surface of the plate with a pre-etch solution having dissolved therein a polyvalent salt of a metal selected from the group consisting of zinc, nickel, calcium, copper, cobalt, iron, lead, magnesium, cadmium, barium, manganese and aluminum in an amount within the range of 2 to 30% by weight, a hydrophilic colloid present in an amount within the range of 0.2 to 5% by weight and inert colloidal solids suspended in the pre-etch solution in an amount within the range of 0.5 to 5% by weight and a surface active agent, and thereafter treating the surface with an acidic etch solution containing an anion which reacts with the metal cation of the pre-etch to form a relatively insoluble precipitate and selected from the group consisting of phosphoric acid, oxalic acid, sulphuric acid, chromic acid, silicic acid, acid ferrocyanide and salts thereof.

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