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LITHOGRAPHIC PRINTING PLATES AND COATINGS THEREFOR

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FIG. 1.

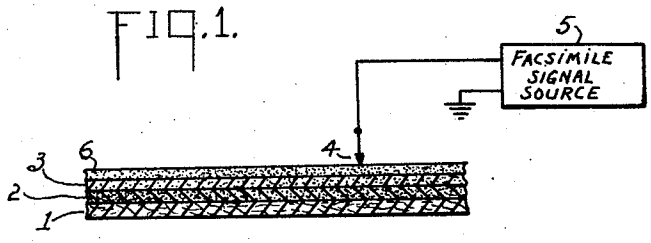
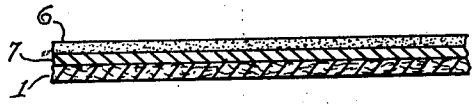


FIG. 2.



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LITHOGRAPHIC PRINTING PLATES AND COATINGS THEREFOR

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7 Claims. (Cl. 101—149.2)

This invention relates to planographic printing plates, and to methods of manufacture thereof.

A principal object of the invention is to provide an improved planographic printing plate of the cellulosic base or backing kind which can be imaged or recorded thereon either by electric voltages acting thereon such as fassimile electric signals, or mechanically such as by writing, typing or printing directly thereon. Planographic plates of the first kind are known in the art as electro-responsive plates, and plates of the second kind are known in the art as direct image plates. Either kind of plate can be used as a master in any well known offset planographic printing press or duplicator mechanism.

As is well known in the lithographic or planographic printing art, the lithographic surface must be such that it will be receptive to fatty and greasy lithographic inks and imaging materials and yet, through proper treatment with repellent solutions used on lithographic presses and duplicators, be capable of being made repellent to these same fatty and greasy materials. At the same time, the lithographic surface must be flexible, water insoluble, and resistant to the action of common solvents. It must also be resistant to the water and oils present in finger prints so that the surface is not easily damaged by handling. The entire plate should, of course, be dimensionally stable and possess a degree of wet strength since it will be in constant contact with aqueous repellent solutions used on lithographic presses. It should also be capable of producing clear sharp copy in required amounts.

According to the present invention we have found that certain salts of hydrolized polyacrylonitrile and some of the reaction products of those salts impart to the lithographic coating the desirable properties. Thus, they produce a lithographic coating which adeheres firmly to the various layers underneath, and one which is insoluble in water and organic solvents. The lithographic coatings produced from these materials are in addition hydrophilic, while being easily imaged by direct mechanical action or by the action of electric voltages thereon.

Accordingly another object of this invention is to provide an improved planographic or lithographic printing surface.

In accordance with the present invention, and referring to the drawing,

Fig. 1 is a cross-sectional view of an electro-responsive planographic plate.

Fig. 2 is a cross-sectional view of a planographic plate of the mechanically responsive or direct imaging kind.

The electro-responsive plate of Fig. 1 employs a sheet of wet strength paper 1, which is a bleached kraft paper which has been sized with either urea or melamine formaldehyde resins. In the case of an electro-responsive plate, the first or base coating 2 applied to sheet 1, is an electrically conductive coating which not only acts as a water barrier to keep the repellent solutions used on planographic printing presses from reaching the paper,

but also serves to direct the current and potentials applied to the plate by means of a stylus, from any well known source of telefacsimile signals and the like, so that the plate is correctly imaged in the desired successive elemental areas. A typical formulation for such a coating has been set forth in our copending application Serial No. 494,683 filed March 16, 1955, and such typical formulation is as follows:

Example 1

30.0 grams of vinylite VYNS (a vinyl chloride-vinyl acetate copolymer, 90% chloride, average molecular weight 15,000, made by Bakelite Corp.)
30.0 grams of aceylene black (Shawinigan Products Corp.)
400.0 grams of methyl ethyl ketone

The above described base coating 2 is applied over the surface of the paper 1 by any conventional means such as by roller coating, brush coating, knife coating, air knife coating, spraying, dipping, wire wound bar coating, and the like. Approximately 1 to 3 pounds per 24 in. by 36 in., 500 sheet ream, is applied. The coating is then heated in a suitable chamber to drive off the solvent.

Over the base coating 2 is applied an electrically conductive intermediate coating 3 the primary purpose of which is to aid in the accurate directing of the currents and potentials which are applied to the recording stylus 4 from any well known source 5 of electric facsimile signals, so that the image appears in the correct portions of the plate. A typical formulation and method of preparing such an intermediate coating has been set forth in our said copending application Ser. No. 494,683. Another formulation incorporating silica is as follows:

Example 2

20 grams Gelva C–3 V–30 (modified polyvinyl acetate, made by Shawinigan Products Corp.)
20 grams Elvanol 20–105 resin (polyvinyl alcohol, made by E. I. du Pont de Nemours Co.)
280 grams methanol
21.33 grams gas black (Dixie #5, by United Carbon Co.)
2.67 grams acetylene black (by Shawinigan Products Corp.)
56 grams Aroclor 1268 (solid chlorinated diphenyl, by Monsanto Chemical Co.)
60 grams Ludox (colloidal silica by E. I. du Pont de Nemours Co.)

In Example 2 the colloidal silica may be replaced in whole or in part by finely divided clay, diatomaceous earth and the like.

This coating 3 is applied by any of the methods mentioned above and is heated in a suitable chamber to drive off the solvent. The amount of this coating should be from 3 to 6 pounds per 24 by 36 inch—500 sheet ream.

The novel lithographic coating 6 according to the invention, is applied over the conductive intermediate coating 3. A typical formulation for coating 4 is as follows:

Example 3

8 grams "Cyanamer" 370 (hydrolyzed polyacrylonitrile polymer, manufactured by American Cyanamid Co.)
152 grams water
24 grams zinc oxide
24 grams zinc sulfide

The "Cyanamer"—370 polymer is dissolved in the water. That solution is then poured into a ball mill jar to which has been added the zinc pigments. The material is then rolled on a ball mill for a period of 24 hours. The coating 4 is then applied over the intermediate coating 3, by any of the conventional methods as for example, reverse roll coating, brush coating, air knife coating, wire

wound bar coating, spraying etc. The material is then passed through an oven whose temperature is high enough to evaporate the solvent, which in this instance is water. The amount of coating 4 which is applied is from 1 to 8 pounds per 24 by 36 inch—500 sheet ream.

At this stage, the polymer and the lithographic coating are still water soluble and as such are useless. That is because the polymer at this stage is a sodium salt, the sodium being present as a result of the alkaline hydrolysis of polyacrylonitrile to form the hydrolized water soluble material.

We have found that the polymer and the lithographic coating can be adequately insolubilized by washing the coating with a solution of heavy metal salt in water. The concentrations satisfactory for this operation vary between 5% and 25%. In this instance we have found a 10% solution of ferric chloride is satisfactory. Other metal salts which we have found to be useful are those of aluminum, calcium, cadmium, copper, barium, zinc, lead, cobalt, tin, nickel, mercury, and chromium.

The reaction between the hydrolyzed polyacrylonitrile and the heavy metal salt is very rapid, so that the lithographic coating remains intact. After the application of the heavy metal salt solution, the plate is heated to drive off the water. At this stage the lithographic coating takes on all the desirable properties outlined hereinabove. An electro-responsive planographic printing plate made in this manner is capable of producing an edition of several thousand copies.

In the case of a direct or mechanically produced image lithographic printing plate according to the invention, the construction thereof as examplified in Fig. 2, is somewhat simpler. Here again we start with a wet strength bleached kraft paper 1, and apply over it a coating 7 designed to keep water or repellent solutions used on lithographic presses or duplicators, from reaching the paper fibres, since that would cause a loss in dimensional stability of the plate. Many such coatings are known in the art. A coating which has been found satisfactory is as follows:

Example 4

10.0 grams Casein (grade B–1, Borden Company)
0.63 gram "Dowicide" G (Pentachlorophenol, manufactured by The Dow Chemical Co.)
60.0 grams clay ("Lustra" clay manufactured by Southern Clay Inc.)
1.0 cc. 28% ammonia
15.0 grams 20% dispersion of defoamer "Nopco" 1497V (manufactured by Nopco Chemical Co.)
210.0 grams water
21.0 grams Dow latex 512K (styrene-butadiene latex, 60% styrene manufactured by The Dow Chemical Co.)

The coating 7 is prepared by soaking the casein in water for one-half hour. The dispersion is heated to 65 degrees C., and the ammonia is added. When the casein dissolves, the solution is cooled and poured into a ball mill jar. Also added to the jar, are the clay pigment, "Dowicide" G, and "Nopco" 1497V. The jar is rolled on a ball mill for 24 hours. Prior to use, the latex is stirred in with mild agitation. This coating 7 may be applied to the paper by any of the means mentioned in Example 3. The coating is then heated to drive off the solvent, which in this instance is water. The amount of coating 7 that is applied is from 8 to 12 pounds per 24 by 36 inch—500 sheet ream. The lithographic coating 6 is applied directly over the base coating 7, and this lithographic coating composition, as well as its method of application, and treatment, is the same as that hereinabove set forth in Example 3.

The hydrolyzed acrylonitrile polymer used in the lithocoating 6 acts as an effective binder for the said pigments, and produces, in conjunction with the pigments, the desired lithographic properties, namely receptivity to the greasy lithographic ink, except in those areas which are rendered ink repellent by the action of the well known repelling solutions of the lithographing press. The pigment-to-binder ratio in the lithographic coating of Figs. 1 and 2 may vary, in weight, from one part pigment and one part binder, to fifteen parts pigment and one part binder. If desired, in some cases it may be found advantageous to add an auxiliary binder to the coating solutions, for example to increase the viscosity. Examples of such auxiliary binders are as follows: alginates, pectates, polyvinyl alcohol, carboxymethyl cellulose, methyl cellulose, etc. These are used in such proportions as to give the desired viscosity for proper coating.

A formulation making use of such auxiliary binders is as follows:

Example 5

8 grams "Cyanamer" 370 (hydrolyzed polyacrylonitrile polymer manufactured by American Cyanamid Co.)
152 grams water
1 gram "Superloid" (ammonium alginate manufactured by Kelco Company)
24 grams zinc oxide
24 grams zinc sulfide

This coating would be used in the same manner described under Example 3.

It is possible to eliminate the use of the insolubilizing wash by including the heavy metal salt right in the coating solution in such a way that it can act only when required to coagulate or insolubilize the "Cyanamer" 370. One such way is to use the ammonium salt of "Cyanamer" 370 and dissolve the ferric chloride in this solution. Upon heating, the ammonia as well as the solvent (water) is driven off. The iron salt immediately reacts with the "Cyanamer" 370 so that the resultant coating becomes insoluble. An example of such a formulation and a method of preparation is as follows:

Example 6

5 grams "Cyanamer" 370 (hydrolyzed polyacrylonitrile manufactured by American Cyanamid Co.)
420 grams water
20 cc. 28% ammonia
5 grams ferric chloride hexahydrate
15 grams zinc oxide
15 grams zinc sulfide

The "Cyanamer" 370 is dissolved in 210 grams of water. After solution takes place the ferric chloride, which has been dissolved in 50 grams of water is added. This causes the "Cyanamer" 370 to gel with a resultant increase in viscosity. This operation should take place under a high speed agitator to make the gel particles as small as possible. The ammonia is then added and when it has been stirred in the rest of the water is added as well. Agitation is continued until the last traces of gel dissolve. This material is then poured into a ball mill jar, the pigments are added, and the jar rolled 24 hours. This coating can be applied over the intermediate coating of electro-responsive planographic printing plates, or over the water barrier base coating of direct image planographic plates by any of the methods heretofore described. Upon heating, the solvent and ammonia are driven off leaving behind an insoluble lithographic coating with desirable properties previously enumerated.

What is claimed is:

1. An electro-responsive planographic printing plate, comprising a flexible backing of a non-conductive material having an exposed lithographic surface coating containing hydrolyzed acrylonitrile polymer, and an intermediate electrically conductive coat.

2. An electro-responsive planographic printing plate, according to claim 1 in which said intermediate coating comprises powdered carbon and a binder.

3. An electro-responsive planographic printing plate

according to claim 1 in which said intermediate coating comprises two strata one of which contains a higher percent of carbon than the other.

4. An electro-responsive planographic printing plate according to claim 1, in which said intermediate coating also includes colloidal silica.

5. An electro-responsive planographic printing plate according to claim 1, in which said intermediate coating also includes finely divided clay.

6. An electro-responsive planographic printing plate according to claim 1, in which said intermediate coating also includes diatomaceous earth.

7. An electro-responsive printing plate having a cellulosic flexible backing, an exposed lithographic surface coating containing a pigment and hydrolyzed acrylonitrile polymer, and an electrically conductive coating between said surface coating and said backing, said conductive

coating acting as a water barrier between said surface coating and said backing, and also as a current director for electric currents which are stylus-applied to said surface coating.

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