United States Patent Office

2,724,665

Patented Nov. 22, 1955

2,724,665

STARCH-COATED PAPER-BASE MASTERS FOR PLANOGRAPHIC PRINTING

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No Drawing. Application April 17, 1953,

Serial No. 349,556

5 Claims. (Cl. 117—155)

This invention relates to the production of coated paper-base planographic printing masters or plates, the coating of which contains a hydrophilic but insolubilized modified starch adhesive.

In planographic printing the design to be reproduced is neither intaglioed nor raised above the plate surface but is substantially level therewith. The design to be reproduced is fixed on the plate surface as a water-repellent image, usually greasy, waxy or resinous in nature. Water or aqueous lithographic solution is applied to the image plate and wets the unimaged areas, making them ink repellent, but does not wet the water-repellent image. An inking-roll now passed over the surface leaves no ink on the water-wet background areas but does leave ink on the imaged areas which can thereafter print the image in reverse on any ink-receptive surface brought into contact therewith. In practice the image is usually first printed upon an offset blanket from which it is transferred to paper so that the final print is identical with the design of the plate.

In business offices it is very frequently necessary to provide from 20 to 50 copies of letters, data sheets, reports and the like. At present it is generally conceded that the most satisfactory means of producing such duplicate copies is a rotary offset duplicator. Relatively expensive metal plates can be used in such duplicators, but office personnel usually find paper-base plates easier to prepare and manipulate. There are on the market several very excellent coated paper-base planographic printing plates or masters. Such coated paper masters in general contain a hydrophilic, water-insoluble hydrophilic colloid such as specially treated casein, a heavy metal-carboxymethylcellulose compound, or a polyvinyl alcohol which is per se insoluble in cold water or has been rendered so by appropriate treatment as with a bichromate. Such masters, though very considerably less costly than metal plates, are nevertheless relatively expensive to produce, so that their cost may be a considerable factor in the expense of producing small lots of duplicates, say in the order of 25. Thus, it is apparent that there is a need for a less costly master designed for use in duplicating small lots of from 25 to 50 copies.

Parchment paper, e. g. paper which has been treated with strong sulfuric acid, is relatively low in price and is sometimes used for masters for this purpose. Fairly satisfactory prints may be obtained therewith, but such parchment plates give a great deal of trouble because they curl quickly and badly and also tend to wrinkle while in use on the duplicator. Consequently, parchment paper plates, in spite of their low cost have in very large measure been replaced by more expensive coated paper plates which are easier to handle.

The minimum requirements for an acceptable short-run coated paper planographic printing plate may be stated as follows:

1. The dry plate must readily accept an oleophilic image and must retain the image during the useful life of the plate.

2. Errors in the image must be capable of being erased with a rubber eraser, and the erased area must be capable of accepting a new image.

3. The imaged plate when properly wet out with aqueous lithographic solution should immediately print legible copies with a clean background, and it should continue to print at least 100 satisfactory copies.

4. The wet plate should lie reasonably flat and it should be dimensionally stable enough so that it will not wrinkle in use.

5. The plate should be relatively low in cost. It has now been found that a plate having the before enumerated minimum requirements can be produced by coating a paper web with an aqueous coating composition comprising mineral pigment, water-soluble adhesive comprising partially hydroxyalkylated starch, i. e. hydroxyalkyl ether of starch, and an insolubilizing agent for said starch adhesive. Why a water-soluble hydroxyalkylated starch should give results quite different from other available starch adhesives is not at present clear. It may be that this modified starch has somewhat better film-forming properties than starch adhesives such as oxidized starch or British gum. On the other hand it may be that the hydroxyalkylated starch is more easily insolubilized by one of the amino-aldehyde resins which are the preferred insolubilizing agents for use according to the present invention. Whatever the correct explanation may be, the fact is that use of the hydroxyalkylated starch as disclosed herein yields results quite different from results given by other starch adhesives in respect to planographic printing qualities.

Partially hydroxyalkylated starch adhesives suitable for use may be produced by treatment of starch according to the disclosure of U. S. Patents 2,516,632 or 2,516,633 of Kesler et al. Examples of suitable starch adhesives produced by ethylene oxide treatment of starch are the "Penford gums," so-called, sold by Penick and Ford, Ltd., Inc., and considered to be hydroxyethylated starch.

For short-run coated paper planographic printing plates there is no necessity for taking steps specifically to increase the wet-strength of the paper base. It is necessary however, that cellulose fibers from the paper base shall not project through the hydrophilic layer of coating which forms the printing surface of the plate. Severe beating or "hydration" of the paper-making furnish will yield a sheet free from projecting fibers, but such a sheet is liable to give trouble from curling. Hence, a preferable procedure is to cement down any loose or projecting fibers by means of a surface application of adhesive material prior to application of the final hydrophilic coating which forms the planographic printing surface.

There may be used to cover over and stick down projecting fibers a water-insoluble base-coating which may, if desired, be of composition the same as or different from the subsequently applied coating which forms the hydrophilic planographic printing surface. Or if desired, an application of surface-size can be used to stick down the fibers, such as a starch surface-size which also contains an agent to insolubilize the starch. A very satisfactory surface-size for the purpose is provided by an ammoniacal solution of casein made slightly acidic by addition of formaldehyde.

A convenient weight of paper base to use for such short-run plates is from 50 to 60 pounds per ream of 500 sheets cut 25 x 38 inches in size. Suitable paper may be produced from a paper-making furnish containing a mixture of chemical wood pulp made from both coniferous trees and deciduous trees, a minor quantity of clay filler, and a small proportion of rosin-size and alum. Such paper when surface-sized, dried, and calendered may then be coated with an aqueous coating composition containing mineral pigment and a lesser quantity

of starch adhesive prepared from starch which has been treated with ethylene oxide to produce the planographic printing plate of the invention.

Since only one side of a printing plate is used for reproduction, from the viewpoint solely of printing it is not necessary to give any treatment to the reverse side of the paper base. As a practical matter, however, in order to minimize any tendency of the sheet to curl and in general to give better stability to the sheet it is desirable to apply a coating of some kind to the reverse side of the paper base. It is likewise advisable to use for this purpose a coating which is relatively water-insoluble so that if in use it inadvertently becomes wetted it will not stick to the plate cylinder by which it may be supported in a printing press. The exact composition of the backcoating is of little importance. A very satisfactory coating is about 10 pounds, dry weight per ream, of the following compositions:

	Parts
Paper-coating clay	100
Starch adhesive (enzyme-converted)	30
Dimethylol-urea	6

Phosphoric acid sufficient to reduce pH to about 5.5.
Water to make solids content about 40%.

The coating to provide the hydrophilic planographic printing surface on the plate of the invention may suitably be applied in amount ranging from about 10 to 20 pounds, dry weight, per ream. Any conventional coating machine may be used for its application; an air-knife coater is very satisfactory. The coating material is applied in the form of an aqueous slurry containing clay or other inert mineral pigment and a lesser quantity of adhesive material comprising partially hydroxyalkylated starch such as that produced by treatment of starch with ethylene oxide according to Patent 2,516,632 or 2,516,633 before mentioned.

An embodiment of the invention is a surface-sized sheet of the character previously described and having a basis weight of 57 pounds per ream, which carries on one side a coating amounting to 10 pounds, dry weight, per ream deposited from an aqueous coating mixture of the following composition expressed in parts by weight:

Paper-coating clay	100
Penford gum No. 280 (ethylene oxide treated starch)	40
Melamine-formaldehyde condensate (Parez 611)	14
Monochloracetic acid (to control pH at about 5.5)	1.5
Propyl alcohol (foam dispersant)	25

Water to make solids content about 26%.

The coated paper was force dried and supercalendered.

The plate described can then be typed upon with a typewriter using a greasy ribbon or it can be imaged in other ways, as by a crayon, greasy pencil, or pen using an oily ink. The imaged plate should then be thoroughly wet by liberal application thereto of an aqueous lithographic wet-out solution carefully applied as by means of a swab of cotton or pad of molleton cloth. When once properly wet-out the plate will thereafter, when used on a rotary offset duplicator, print clean and legible copies immediately and will continue to do so for at least 500 copies.

The quantity of ethylene oxide treated starch used in the coating composition per pound of mineral pigment will vary depending upon the particular pigment being used, the particular paper stock to which it is being applied, and the number of copies that are required to be printed from the finished plates. Obviously sufficient adhesive must be used to bind the coating to the base with sufficient force so that it will not be pulled away from the base by the tack of the printing-ink on the press. About 25 parts of the hydroxyalkyl ether of starch per 100 parts of clay is usually considered about

the minimum that can be safely used. As the quantity of the hydroxyalkyl ether of starch is increased the strength of the coating likewise increases, but tendency to trouble from curling likewise increases at the same time. Consequently about 75 parts of the starch adhesive per 100 parts of pigment is about the maximum ever feasible for use. Actually the preferred range will be from about 35 to 50 parts of modified starch to 100 parts of pigment.

The preferred way of insolubilizing the starch adhesives in manufacturing the plate of the invention is to include a significant quantity of water-soluble amino-aldehyde resin in the coating composition. When the mixture is subjected to force-drying with heat the amino-aldehyde resin is said to be "cured," and substantial water-insolubility of the coating results. It seems probable that in the curing process there is some actual reaction between the hydroxyalkyl ether of starch and the resin; otherwise the resulting insolubility of the starch would be difficult to explain. Most of the amino-aldehyde resins cure much more rapidly in the presence of some acidic substance which holds the pH value of the solution appreciably below 7. When using such an acid-curing resin in making the plate of the invention, a so-called "acid-catalyst" is also included in the coating composition.

Among the water-soluble amino-aldehyde resins effective for use are dimethylol-urea, other water-soluble urea-formaldehyde condensates, and water-soluble melamine-formaldehyde condensates. There are some differences among the amino-aldehyde resins in respect to time and/or temperature required for curing. Naturally conditions under which the coated paper is cured or dried will be modified to suit the particular amino-aldehyde resins used to insolubilize the starch. In general, melamine-formaldehyde condensates are preferred; one very satisfactory melamine-formaldehyde condensate is sold as Parez 611 by the American Cyanamid Company.

The ratio of amino-aldehyde resin to starch may be varied considerably. Normally 25% of amino-aldehyde resin based on the weight of the hydroxyalkyl ether of starch may be expected to insolubilize the coating. If the period of curing can be prolonged, even smaller quantities of the resin may give a substantial degree of insolubility. On the other hand, considerably larger quantities of the resin may be used if desired. In fact, a quantity of amino-aldehyde resin up to 100% of the weight of modified starch present may be included in the coating composition without making the resulting coated surface unduly "sensitive" or susceptible to toning. In everyday operation it is convenient to use a weight of amino-aldehyde resin equal to about 35% of the weight of hydroxyalkylated starch present. When melamine-resins are used, under acidic conditions, curing of the resin results from ordinary drying of the coated paper at steam temperature for a period long enough to evaporate the water from the coating, whereas urea-resins may require more heating or a fairly long period of aging at ordinary temperature before they become cured. A typical water-soluble melamine-resin satisfactory for use is made by condensing 1 mole of melamine with 2 moles of formaldehyde.

While any water-soluble hydroxyalkylated starch will give improved results according to the invention, hydroxyethyl starch is at present the most easily obtainable of such starches and is very satisfactory for use. Hydroxyethyl starches of medium to low viscosity are preferred because they are easier to apply than starches of higher viscosity, though the latter may be used if desired. Very satisfactory for use is starch prepared by first treating raw starch to reduce its viscosity, as by conventional acid hydrolysis at a temperature below the gelation temperature of the starch, and then reacting the lowered-viscosity starch with ethylene oxide in amount between the limits of 1% and 5% based on the dry weight of the starch.

Insofar as planographic printing is concerned hydroxyalkylated starch, e. g. starch treated with ethylene oxide as previously described, behaves differently and gives altogether different results than do the ordinary converted starch adhesives of commerce. If, for instance, an enzyme-converted corn starch or a starch gum such as oxidized or chlorinated starch is substituted for the Penford gum No. 280 in the formula previously set forth, paper coated therewith will not be in any degree a useful planographic printing plate. For if an attempt is made to print from such a product on an offset printing press, either the background will accept ink and so print black all over, or if a huge excess of aqueous fountain-solution is used to keep the background clean the image will be obliterated. In either case the plate is utterly useless. With use of hydroxyalkylated starch in the formula, however, the coated product serves excellently as a planographic printing plate, immediately yielding prints with clean background and distinct images and continuously producing them for 100 copies or more.

We claim:

1. A planographic printing plate comprising a paper base and a water-insoluble coating thereon presenting a planographic printing surface, said coating consisting essentially of finely divided mineral pigment and a water-insoluble hydrophilic adhesive component comprising the reaction product of hydroxyalkyl ether of starch and an amino-aldehyde resin, the ratio of said pigment, hydroxyalkyl ether of starch and an amino-aldehyde resin being from about 25% to about 75% of the hydroxyalkyl ether of starch based upon the weight of the pigment, and from about 25% to about 100% of the amino-aldehyde resin based upon the weight of the hydroxyalkyl ether of starch.

2. A planographic printing plate according to claim 1 in which the hydroxyalkyl ether of starch is a hydroxyethyl ether of starch.

3. A planographic printing plate as defined in claim 1 in which the amino-aldehyde resin is a melamine-formaldehyde condensate.

4. Process of making a planographic printing plate which comprises coating a paper base with an aqueous slurry consisting essentially of water, finely divided mineral pigment, a water-soluble hydroxyalkyl ether of starch and a water-soluble amino-aldehyde resin, the ratio of said pigment, hydroxyalkyl ether of starch and amino-aldehyde resin being from about 25% to about 75% of the hydroxyalkyl ether of starch based upon the weight of the pigment and from about 25% to about 100% of the amino-aldehyde resin based upon the weight of the hydroxyalkyl ether of starch and drying and supercalendering the coated paper base under conditions capable of curing the resin.

5. A planographic printing plate as defined in claim 1 in which the hydroxyalkyl ether of starch is the product obtained by subjecting starch to acid hydrolysis at a temperature below its gelation temperature to reduce its viscosity and then reacting it with from 1% to 5% of ethylene oxide based upon the dry weight of the starch.

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