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PRINTING MASTER WITH BASE OF KETENE DIMER SIZED PAPER

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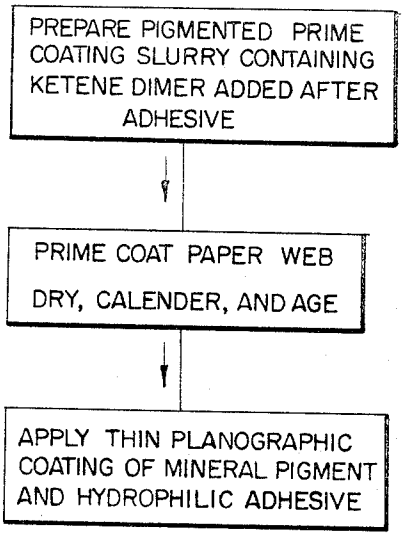


FIG. 1

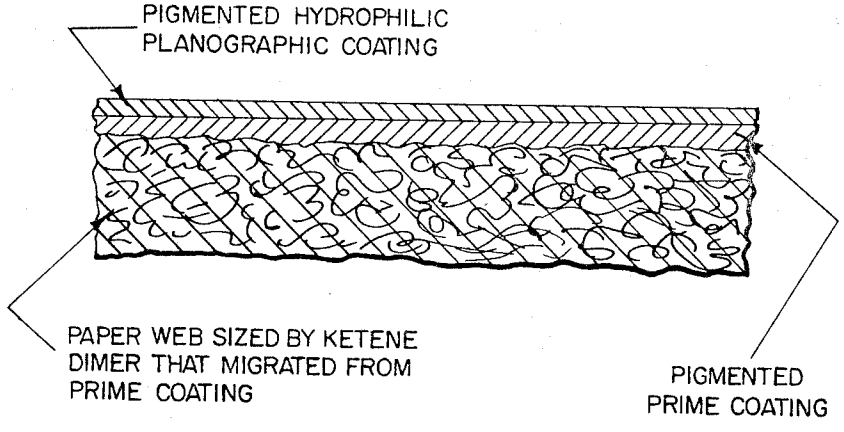


FIG. 2

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PRINTING MASTER WITH BASE OF KETENE DIMER SIZED PAPER

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This application is a continuation-in-part of Ser. No. 836,598, Planographic Printing Master and Backing Sheet Combination, filed Aug. 28, 1959 by the present inventors and now forfeited.

This invention relates to planographic printing and more particularly to the preparation of a sized and surface coated cellulosic body stock for use as a planographic printing plate or master.

Planographic masters need to meet several important requirements. The top surface of the master should be capable of supporting a film of lithographic fountain solution in the background areas around the inked letters or indicia to be printed. If the background areas do not hold a continuous film of fountain solution the lithographic ink will adhere at random to the surface of the plate and "toning" results. The fountain solution should not penetrate into the body stock. Absorption of fountain solution into the body stock not only makes it more difficult to retain the fountain solution on the surface of the master, but it also tends to weaken the master and cause the ink receptive letters to be undermined or dislodged from the surface of the master.

The general construction of planographic masters in the past has included a heavily sized body stock protectively coated on both sides with at least one coated surface being suitable for planographic printing. The sizing agent for the body stock has traditionally been rosin. As is well known, rosin is an effective sizing agent, but it has a peculiar property which renders it particularly harmful to planographic printing. Wherever oleophilic rosin appears at or near the surface of the master, the fountain solution is driven away and the printing ink adheres to the sheet near the rosin causing toning. Because of this, it has been necessary to make the coating on the conventional master quite thick to smother the hydrophobic qualities of the rosin. Also, because the masters must necessarily be stacked or wound on rolls at various points during manufacture, shipment, and storage, it has been necessary to apply a protective coating to both sides of the master in order to prevent rosin from the body stock on one sheet from transferring to or affecting the coated surface of a contiguous master. In addition, it has also been a problem in the industry to make the printing surface sufficiently thick and/or continuous to avoid exposing the rosin in the body stock to the lithographic ink and thereby adversely affecting the printing qualities of the surface of the master.

Accordingly, a major object of our invention is to provide a combined sized body stock and planographic printing surface which is oleophilic when dry so as to receive and hold an oil-based ink printed thereon, but when wet will be more hydrophilic than oleophilic in the background areas so that the fountain solution can form a continuous aqueous film over the background areas. Another object is to provide such a planographic master in which the body stock is sized sufficiently to prevent rapid water penetration, which avoids the requirement of a special coating on the back side of the plate, and which is not adversely affected by small imperfections in the printing surface.

In this invention a paper web body stock is sized with a dimer of an aliphatic ketene having in the range of 6 to

20 carbon atoms per molecule. The dimer is applied through the agency of a pigmented prime coating. After the coating has been dried and calendered, a thin coating of a suitable pigmented hydrophilic planographic composition is supplied.

The use of ketene dimers as sizing agents for papers has been previously suggested. These dimers are known as extremely potent sizing agents. Since they are extremely active and hydrophobic, however, it is believed that the art has not appreciated that a paper sized with a ketene dimer could serve as a base for making a planographic master.

The amount of dimer used in this invention is quite small, in the range of 0.07 to 0.30 weight percent on the cellulosic fibers of the paper web. This assures that no excess is present that might migrate into and interfere with the performance of the pigmented hydrophilic top coating. The ketene dimer is applied to the cellulosic web in admixture with the prime coating composition rather than directly to the web. This is believed to at least in part account for the improved performance of the master of this invention because some residual amount of ketene dimer remains in the prime coating while the remainder migrates into and effectively sizes the cellulosic web. The ability of such a small amount of ketene dimer to migrate into and effectively size a paper web from a coating composition has not previously been known. In this connection, the order of addition of the ketene dimer to the prime coating composition is critical because of the small amount that is used. The pigment of the prime coating composition will absorb or pick up on its surface the other ingredients of the coating composition. If the ketene dimer is added to the slurry of the pigment before the adhesive binder, most of it is irreversibly absorbed by the pigment and is not free to migrate. In the present invention, a water dispersible adhesive binder is first admixed with the slurry of the pigment of the prime coating so that the pigment is first coated with the adhesive. Thus, when the ketene dimer is added it is not lost to the pigment and is free to migrate into and size the cellulosic fibers of the paper web.

The heretofore unappreciated and excellent properties of the prime-coated, ketene-dimer-sized paper web permits a relatively thin coating of the pigmented hydrophilic top coating to be used. In the range of 3 to 15 pounds (dry weight) per ream (500 sheets; 25 x 38 inches) has been found to be satisfactory. The top coating can contain any suitable water dispersible hydrophilic adhesive and mineral pigment. Adhesives of the colloidal type are preferred.

This manner of applying the ketene dimer sizing agent results in a base or surface under that top planographic surface that is less oleophilic than the top surface. Careful and expensive preparation of the base before application of the top coating is not required. Breaks or holes in the top coating expose areas that are less oleophilic and that will not accept ink and thus remain clean.

The top coating may be so thin therefore as in some cases not to be continuous. It has been found that despite the strong power of the ketene dimer to size the sheet, the dimer does not tend to rupture the film of fountain solution covering the background areas in use even though the master is only lightly coated with the planographic master coating and even though the coating may not be uniformly continuous across the face of the sheet.

In the case of rosin sized sheets, the rosin is less firmly fixed in the web. The particles are merely held physically instead of being chemically combined with the cellulose. Aging of a rosin sized web sometimes causes the rosin to migrate or sublime in some manner through the top coating and interfere with its performance. This does not occur with a sheet sized with a small amount of

ketene dimer applied through the agency of a prime coating.

The drawings attached to and forming a part of this specification and the following examples will serve to make this invention clearer. In the drawings, FIGURE 1 schematically depicts the process of this invention, and FIGURE 2 illustrates in an enlarged cross-section view the improved planographic master.

EXAMPLE I

An unsized paper web was made containing 50 parts each of bleached wood fibers from coniferous trees and 50 parts of bleached wood fibers from deciduous trees and 15 parts of finely divided calcium carbonate filler. The web weighed about 52 pounds per ream. The unsized cellulosic paper webs used in the practice of this invention have preferably a weight in the range of 45 to 80 pounds per ream. The web of this example was coated on the paper machine, on both sides, by a squeeze-roll coater with 3 pounds per side, dry weight, of a priming coat mixture prepared as follows:

Penford gum 280 (47.5 parts), dimethylol urea (2 parts), sodium carbonate (0.12 part) and water (110 parts) were all cooked together (as disclosed in U.S. Patent 2,555,057). The cooked preparation was mixed with a pigment consisting of fine coating clay (90 parts) and finely divided calcium carbonate (10 parts). Thereafter an emulsified dimer of hexadecenyl ketene (2.25 parts) and water were added. The amount of water used was sufficient to reduce the total solids content to 32 weight percent. The hexadecenyl ketene dimer is emulsified by the use of ⅛ its weight of Atlox 1096, which is a polyethylene sorbital hexaoleate made by Atlas Powder Company. The amount of ketene dimer applied to the paper web through this coating composition was approximately 0.16 weight percent based on the cellulose fibers.

The so prime-coated web was dried and calendered on the paper machine. It was then allowed to age for 48 hours and was found to be well-sized. Whether this aging to permit migration of the ketene dimer in the web occurs before or after the application of the planographic top coating does not appear to be material.

The prime coated web was thereafter coated on one side with 7 pounds dry weight per ream of a top coating composition having the following formulation (parts by weight):

Fine coating clay	100
Penford gum 280	40
Parez 611	14
Zinc acetate (anhydrous)	40
Monochloracetic acid	3.5
Propanol	30
Water to make solids content	28

Penford gum 280 is a partial hydroxyethyl ether of starch sold by Penick and Ford, Ltd. Parez 611, a product of American Cyanamid Company, is partially condensed melamine-formaldehyde resin. Monochloracetic acid functions as a catalyst or accelerator for the Parez 611. The propanol is used as a wetting and anti-foaming agent.

The thus coated web was dried, heated briefly to 300° C. to cure the resin and water proof the adhesive and was then calendered. The finished coated web was cut into sheets, stacked together with the double-coated side of one sheet in contact with the prime-coated side of the adjacent sheet. The sheets so stacked were artifically aged by being heated at 90° C. for 4 hours.

The sheets were thereafter imaged on the double-coated side with a greasy typewriter ribbon, wet out with an aqueous solution of acid phosphate, and run on a rotary offset duplicator to print over 500 good copies. The background areas remained clear and free from specks and toning, thus showing that no harmful transfer from sheet-to-sheet occurs during aging.

EXAMPLE II

The same prime-coated base as in the previous example was coated on one side with 3 pounds per ream dry weight of the top coating composition which has been further diluted with water to a solids content 20%. The coated paper was then dried, cured for a few seconds at 300° C., and calendered.

There after the paper was cut into sheets, stacked with the double coated side of one sheet in contact with the prime coated side of the adjacent sheets. The stacked sheets were then artificially aged at 90° C. for 4 hours. The artificially aged sheets were imaged upon the double-coated side by use of a typewriter using a greasy ribbon. An imaged sheet was folded to make a crease through the image area. It was then unfolded, wet out with an aqueous solution of acidic phosphate, and run on a rotary offset duplicator. Over 25 good copies were printed therefrom. There was no specking or toning in the background areas. The break in the coating caused by the crease did not reproduce to make a black line or flaw in the copy.

It was not found necessary to increase the ratio of adhesive to pigment as the weight of the phanographic coating used decreased. This is contrary to previous experience. The difference is doubtless due to the fact that in the past the paper base used has itself been so strongly oleophilic that care had to be taken to ensure continuous coverage of the base by a film of the phanographic coating adhesive. Otherwise, toning of the background areas would occur.

In the present case, the prime-coated paper base is as hydrophilic as the planographic top coating. Hence, even if it is not entirely covered with a continuous film, no toning of the background will result.

Other starch adhesives of comparable viscosity such as oxidized starch or enzyme-converted starch may be used in place of the Penford gum 280 in the prime coating formula set forth above.

A feature of this invention is the use of a sized paper base which is free from rosin and which is not more oleophilic than conventional planographic coatings. To such a base there can be applied any coating composition used for surfacing conventional coated paper planographic printing plates or masters. The top coating shown in Examples I and II is very satisfactory, but replacement thereof by any of a great number of such known coating compositions will still give satisfactory results. For instance, the adhesive shown for the top coating formula can be replaced by oxidized starch, carboxylmethylcellulose, polyvinyl alcohol, carboxymethyl-hydroxyethyl cellulose, and many others as set forth in Worthen Patent No. 2,534,650. If casein, soy protein, or other adhesive coagulable by heavy metal salts is used, the zinc acetate should of course be omitted from the coating formula and instead this zinc salt may be washed over the coated surface in aqueous solution. If desired, except in the instance where casein or soy protein is used, the zinc acetate may be omitted from the formula. The resulting product gives satisfactory results.

An example of such a top coating formulation is:

Disperse in 292 units of water 40 units of partially hydroxyethylated starch (e.g. Penford gum 280) and 12 units of a partially condensed melamine-formaldehyde resin (e.g., Parez 605 made by American Cyanamide Company). Heat the mixture to 99° C. and maintain it at 99° C. for about 15 minutes until a sample withdrawn and cooled to 25.5° C. has a viscosity of 800 centipoises as measured on a Brookfield viscometer. Cool the mixture and mix therewith 100 parts of fine particle clay, 100 parts of water, 0.4 part of the sodium sulfate derivative of 7-ethyl-2-methyl undecanol-4, and 0.2 part of tributyl phosphate. The last two ingredients function as wetting and anti-foaming agents respectively.

The ketene dimers used in this invention, namely, dimers of aliphatic ketenes containing from 6 to 20 carbon

atoms, confer water-resistance to the paper, their effectiveness increasing to a slight degree with an increase in the number of carbon atoms. These dimers can be made by reacting a fatty acid in known ways to form an acid chloride and then reacting the acid chloride with a tertiary amine. Various specific dimers are available commercially, although they almost always contain slight amounts of other dimers. The presence of other ketene dimers is not objectionable; in fact, the invention has been found to work just the same where two ketene dimers have been together on a 50-50 basis. Specific dimers that have been found satisfactory are hexadecyl ketene dimer, hexadecenyl dimer, tetradecyl ketene dimer, and dodecyl ketene dimers. Other dimers that are substantial equivalents may be recognized readily by persons skilled in the art.

It is to be noted that the dimer of hexadecenyl ketene is liquid at ordinary room temperature and, therefore, is more conveniently handled than dimers which are solid at room temperature.

The aliphatic ketene dimers are insoluble in water; however, they can be dispersed in water by use of emulsifying agents. Generally speaking any method satisfactory for making aqueous dispersions of paraffin wax can be used to make satisfactory dispersions of the ketene dimers. For example, the ketene dimer can be mixed in hot water with cationic starch or with gum ghatti, and then put through a colloid mill to yield a satisfactory aqueous dispersion. Use of polyethylene sorbitol hexaoleate (1 part per 5 parts ketene dimer as previously described) is another suitable method of dispersing the ketene dimer.

Having described this invention what is sought to be protected by Letters Patents is succinctly set forth in the following claims.

What is claimed is:

1. A process for making a flexible planographic printing master comprising the steps of: preparing a slurry consisting essentially of water, mineral pigment and adhesive binder; thereafter adding to said slurry an emulsified sizing agent consisting of a dimer of an aliphatic ketene having in the range from 6 to 20 carbon atoms per molecule; applying said slurry as a prime coating to an unsized cellulosic paper web having a ream weight in the range of 45 to 80 lbs. to form a surface coating thereon, the amount of said sizing agent being applied thereby being in the range of 0.07 to 0.30 weight percent on the cellulosic fiber content of the paper web; drying the prime coating and thereafter applying a lithographic top coating over said prime coating in an amount in the range of 3 to 15 lbs. per ream (dry weight), said lithographic top coating comprising a slurry of a water dispersible hydrophilic adhesive binder and a coating grade mineral pigment.

2. The process of claim **1** wherein said ketene dimer is the sole sizing agent used for said paper web.

3. A process of manufacturing a planographic printing master, comprising: prime coating a cellulosic paper web with a slurry composition consisting essentially of water, mineral pigment, water dispersible adhesive, and an emulsified ketene dimer sizing agent added thereto after the pigment and adhesive, the amount of said ketene dimer being in the range of 0.07 to 0.30 weight percent on cellulosic fiber; drying the prime coating and thereafter applying a thin hydrophilic planographic top coating thereover.

4. A flexible planographic printing master comprising a cellulosic paper web having a ream weight in the range of 45 to 80 pounds and being free of rosin size but containing as a sizing agent a dimer of an aliphatic ketene having 6 to 20 carbon atoms per molecule; an intermediate layer of a coating consisting essentially of mineral pigment and a hydrophilic adhesive binder sized with said sizing agent, the total amount of said sizing agent present in said paper web and intermediate coating being in the range of 0.07 to 0.30 weight percent on the cellulosic fiber content of said web; and a thin hydrophilic planographic top coating over said intermediate coating in an amount in the range 3 to 15 pounds per ream (dry weight) and comprising a coating-grade mineral pigment bonded with an initially water dispersable hydrophilic adhesive binder that has been rendered insoluble, said intermediate coating being less oleophilic than said top coating.

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