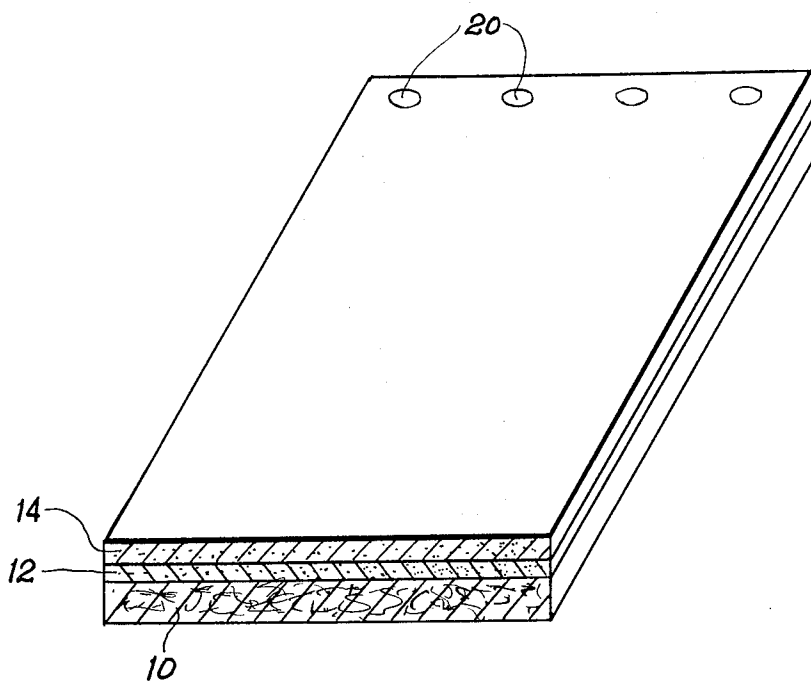


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AND PUCKERING PROPERTIES
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1

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COLLOID COATED PAPER WITH ANTI-WRINKING AND PUCKERING PROPERTIES
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This invention relates to the preparation of coated papers and it relates more particularly to an element incorporated as a component in a coating composition formulated of casein and other hydrophilic colloids to minimize curl, puckering and the like distortions introduced by the coating in response to exposure to elevated temperature and low humidity conditions.

This invention will be described with reference to coated paper lithographic plates wherein the lithographic face coat, or its underlying barrier coat, or both, are formulated to contain casein, such as in the Worthen Patent No. 2,534,560; or an insolubilized polyacrylate, such as in the Beatty Patent No. 2,760,431; or an alginate, as in the Ensink Patent No. 2,806,424; or a carboxymethyl cellulose, as in the Van Dusen Patent No. 2,542,784, or other hydrophilic colloids such as polyvinyl alcohol, starch and the like proteinaceous colloids. Such coatings are formed with or without fillers depending upon their use as a base coat or as a face coat. When such coated papers are exposed to elevated temperatures under conditions of low humidity, as when the coated papers or plates are processed through a fuser or heated section for the fusion of pigment particles deposited on an electrostatic image for the development of copy, as in a "Xerox" copy process, the coated papers tend to curl or pucker with the result that they become less suitable for use as copy and unsuitable for use as a master in the preparation of multiple copies therefrom. They also become more difficult to file by comparison with sheets that are otherwise flat.

Thus it is an object of this invention to produce and to provide a composition for producing papers coated with proteinaceous materials and in which the tendency to pucker or curl is markedly reduced, if not completely eliminated, especially in response to exposure to elevated temperature in an atmosphere of low humidity, and it is a related object to produce and to provide a method for producing coated paper lithographic plates which are substantially free of curling when exposed to elevated temperature and/or low humidity, as in a fuser for development of the powdered electrostatic image in an electrostatic copy process or when exposed to a temperature such as in excess of 350° F.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing, in which

The figure of the drawing is a perspective view partially in section of a conventional coated paper lithographic plate of the type with which this invention may be practiced.

The coated paper lithographic plate illustrated in the figure of the drawing comprises a paper base sheet 10 which may be formed of paper sheet stock, preferably embodying a small amount of a resinous binder, such as urea formaldehyde, melamine formaldehyde, and the like in the pulp slurry to produce a high wet strength paper.

2

It is preferred to fabricate the plate with a barrier coat 12 intermediate the base sheet 10 and the face coat 14. The barrier coat is used to anchor the face coat more securely to the base sheet and to enhance the wet strength of the assembly and thereby the number of copies that can be produced from the coated lithographic plate.

The face coat 14 is usually formulated to contain an insolubilized hydrophilic colloid or proteinaceous material, such as casein, starch, polyvinyl alcohol, alginate, polyacrylate, carboxymethyl cellulose, and the like, in combination with a filler such as satin white, zinc oxide, clay and the like. Face coats formulated of casein may be selected from the Worthen Patent No. 2,534,650, of which the following is representative:

EXAMPLE 1

	Parts by weight
Pigment (clay) (finely divided) -----	100
Hydrophilic adhesive base (casein) (in a water solution of ammonia) -----	17.5
Dimethylol urea (to insolubilize the casein) ----	1.75

The face coat of the above formulation may be applied onto the base sheet previously coated with the barrier coat or the face coat composition may be applied directly onto the base sheet in the absence of a barrier coat to produce a coated paper lithographic plate.

A representative face coat formulated of a polyacrylate may be selected from the Beatty Patent No. 2,760,431, of which the following is representative:

EXAMPLE 2

	Parts by weight
Clay -----	180
Zinc oxide -----	18
Polyacrylic acid (25% by weight solution in water) --	160
Concentrated ammonium hydroxide -----	100
Water -----	100

The foregoing composition contains about 40% by weight of solids and may be applied in coating weights of 8-10 pounds per 3000 square feet of surface area of a base sheet followed by air drying. The face coat may be applied with or without a barrier coat. A suitable barrier coat would have the same formulation but with the absence of the clay component.

A suitable face coat formulated of alginate may be selected from the Ensink Patent No. 2,806,424, of which the following is representative:

EXAMPLE 3

	Parts by weight
Sodium alginate -----	3
Zinc chloride -----	0.012
Barium sulphate -----	18
Water -----	79

After the foregoing coating composition has been applied to the base sheet, the coating may be further insolubilized by treatment with a wash coat containing from 1/2-5% by weight of aluminum chloride or zinc chloride.

A representative coating formulated of carboxymethyl

cellulose may be selected from the Van Dusen Patent No. 2,542,784, of which the following is representative:

EXAMPLE 4

	Parts by weight
High viscosity aluminum salt of carboxymethyl cellulose (1% solids) -----	20
28% by weight ammonium hydroxide -----	10.4
Finely divided hydrated alumina -----	12

The face coats can be applied in the manners described in the aforementioned patents without a barrier coat; however, when a barrier coat 12 is employed intermediate the base sheet and the face coat 14, the barrier coat may be formulated of materials similar to those employed in the corresponding face coat but preferably with less filler and with a higher degree of cure or waterproofing. Suitable barrier coats are described in various of the aforementioned patents, such for example as in the Worthen Patent No. 2,534,650.

Offset or lithographic plates of the type prepared in accordance with the teachings of the aforementioned patents and by the compositions of Examples 1-4 remain fairly smooth and flat when processed under normal conditions for imaging the plate with an oleophilic imaging material applied either by typewriter ribbon, ink stylus, crayon or printing press. However, considerable utility has developed in the use of such coated paper plates imaged from an original by the use of the electrostatic concepts of the Carlson Patents No. 2,297,691 and No. 2,357,809, or the Mayo Patents Nos. 3,062,108, 3,062,109 and 3,062,094, and referred to commercially as the "Xerox" process.

In the electrostatic process, an electrostatic image of the original is formed either on a selenium metal drum or on the surface of the coated paper plate. The latent electrostatic image is developed by a loose powder which is attracted to the image by a tribo-electric effect, the powder being formulated to contain a dyestuff or pigment mixed or otherwise combined with a fusible resinous or oleophilic material. The developing powder is retained by the latent electrostatic image and transferred from the drum onto the surface of the coated paper plate or otherwise collected directly on the plate surface when the latent electrostatic image is developed directly thereon. The next step is to fuse the powder image on the surface of the coated paper and, for this purpose, the coated paper is exposed to a temperature of about 400-450° F. for a matter of about 1-30 seconds. In addition to the elevated temperature to which the sheet is exposed, the atmosphere is usually at relatively low humidity.

It is as the result of the exposure of such coated papers to the elevated temperature and low humidity of the fuser that is believed to cause curling and puckering to take place in the imaged plate issuing therefrom. Such curled or puckered plate is difficult to handle. It is difficult to mount on the printing press. It is difficult to make lie flat for wetting and inking during the normal cycles of the lithographic reproduction process with the result that the copy that is secured is of relatively poor quality.

Somewhat to the surprise of applicant, it has been found that the tendency for such coated papers to pucker or curl when exposed to elevated temperature and low humidity can be greatly alleviated if the coating compositions of the types described are formulated to contain in addition one or more polyhydroxy compounds having at least three primary alcohol groups, as represented by trimethylol propane, trimethylol ethane, trimethylol butane, and the like. The results are all the more unexpected since corresponding reductions in curling or puckering of such coated papers are not experienced by the corresponding additions of polyhydric alcohol compounds of the type included within the class of humectants such as glycerine or glycols, as represented by ethylene

glycol, propylene glycol, or such polyhydric alcohol polymers. The polyhydroxy compound may be formulated into the coating composition in an amount corresponding to one part by weight of the polyhydroxy compound to 1-20 parts by weight of the colloid or proteinaceous binder, depending somewhat upon the binder component but more upon the presence or absence of a barrier coat in combination with the face coat. In the absence of a barrier coat, it is desirable to formulate the face coat with the polyhydroxy compound present in an amount less than the colloid binder and preferably in the ratio of one part by weight of the polyhydroxy compound to 5-10 parts by weight of the colloid or proteinaceous binder. In the use of a barrier coat, it is desirable to formulate the barrier coat with a higher concentration of polyhydroxy compound, preferably in the ratio of one part by weight of the polyhydroxy compound per 1-10 parts by weight of the colloid or proteinaceous binder. When employed in combination with a barrier coat containing the polyhydroxy compound in the foregoing ratio, the face coat may be formulated with an amount of polyhydroxy compound within the ratio of one part by weight of the polyhydroxy compound per 10-20 parts by weight of the colloid or proteinaceous binder. The lesser amount of polyhydroxy compound in the face coat, when employed in combination with the barrier coat, suffices to improve the wet-out and the bonding relationship between the face coat and the barrier coat, dependence being had primarily on the polyhydroxy compound in the barrier coat to combat curling and puckering.

The invention may be illustrated by the following example:

EXAMPLE 5

	Parts by weight
Clay -----	180
Zinc oxide -----	18
Polyacrylic acid (25% solution in water) -----	160
Concentrated ammonium hydroxide (25%) -----	100
Water -----	100
Trimethylol ethane -----	5

The foregoing is an example of a face coat composition which may be applied onto a suitable paper base sheet in accordance with the procedures of Examples 1-4 previously described.

The following will illustrate the combination which makes use of a barrier coat and a face coat as multiple coatings on a suitable paper base sheet:

EXAMPLE 6

Barrier coat:	Parts by weight
Water -----	26.0
Zinc caseinate (15.5% solids) -----	70.3
Formaldehyde (37% solution) -----	1.4
Ammonium hydroxide (28% solution) -----	1.2
N-butanol -----	1.1
Trimethylol propane -----	4.0

This is applied at a coating weight of about 4 pounds per 3000 square feet.

EXAMPLE 7

Face coat:	Parts by weight
Clay -----	21.7
Zinc oxide -----	8.7
Ammonium hydroxide (28% solution) -----	3.5
Ammonium polyacrylate (18.5% solution) -----	28.6
Zinc acetate -----	1.5
N-butanol -----	3.6
Water -----	32.4
Trimethylol propane -----	0.5

This is applied at a coating weight of 8-10 pounds per 3000 square feet.

The coating compositions are formulated and applied

in accordance with the procedure described in Patent No. 2,760,431 with the corresponding weights of barrier and face coats.

While the invention has been described with particular reference to the fabrication of coated papers in the preparation of coated paper offset plates, it will be understood that the same concepts will apply to coated papers generally in which use is made of such colloid or proteinaceous binders alone or in combination with fillers or pigments.

Papers coated with compositions of the type described have been found to remain substantially, if not perfectly, flat during normal processing or when processed at elevated temperatures or low humidity, or both. The effect does not appear due to the humectant properties of the specific polyhydroxy compounds because materials normally employed as humectants do not give equivalent results even when used in the same or varying amounts by comparison with the polyhydroxy compounds employed in the practice of this invention. It is known that the polyhydroxy compounds, especially trimethylol propane, appear to be compatible with the binder, such as casein, and are not volatilized off but instead remain or are otherwise retained in the coating throughout the processing of the coated paper in use at temperatures as high as 400-500° F. and under relatively low humidity conditions.

When the invention is practiced in the preparation of a coated paper offset or lithographic plate, it is desirable to fabricate the plate with openings 20 across the leading edge portion for purposes of mounting the plate on the cylinder of a conventional lithographic press. Other means for clamping the plate may be employed.

It will be apparent from the foregoing that I have described a formulation for use in the preparation of coated papers wherein such coatings are not undesirably affected by heat or low humidity to cause wrinkling or puckering such that the coated papers can be processed in techniques employing elevated temperatures and low humidities while remaining relatively flat as a result of such processing steps.

It will be understood that changes may be made in the details of formulations and compositions and their method of application without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A coated lithographic paper plate comprising a paper base sheet having an insolubilized hydrophilic colloid coating on the base sheet containing an organic polyhydroxy alcohol of a lower hydrocarbon containing at least three primary hydroxyl groups in an amount within the range of 1 part by weight of the polyhydroxy alcohol per 1-20 parts by weight of the hydrophilic colloid.

2. A coated paper lithographic plate comprising a paper base sheet and an insolubilized lithographic coating on the surface of the base sheet containing a hydrophilic binder colloid and an organic polyhydroxy alcohol of a lower hydrocarbon containing at least three primary hydroxyl groups present in an amount within the range of 1 part by weight of the polyhydroxy alcohol per 1-20 parts by weight of the hydrophilic binder.

3. A coated paper lithographic plate as claimed in claim 2 in which the coating is in the form of a face coat and in which the polyhydric alcohol containing at least three primary hydroxyl groups is present in the face coat in an amount within the range of 1 part by weight per 1-20 parts by weight of the hydrophilic binder.

4. A coated paper lithographic plate as claimed in claim 2 in which the coating is in the form of a barrier coat and in which the polyhydric alcohol containing at least three primary hydroxyl groups is present in an amount within the range of 1 part by weight per 1-10 parts by weight of the hydrophilic binder.

5. A coated paper lithographic plate as claimed in claim 1 in which the hydrophilic colloid is selected from the group consisting of casein, alginates, carboxymethyl cellulose, polyacrylic acid, polyvinyl alcohol and starch.

6. A coated paper lithographic plate comprising a base sheet, an insolubilized face coat on one side of the base sheet containing a hydrophilic colloid and a polyhydroxy alcohol of a lower hydrocarbon containing at least three primary hydroxyl groups, and a barrier coat between the face coat and the base sheet containing a hydrophilic colloid and a polyhydroxy alcohol containing at least three primary hydroxyl groups wherein the polyhydroxy alcohol containing at least three primary hydroxyl groups is present in the barrier coat in an amount within the range of 1 part by weight thereof to 1-10 parts by weight of the hydrophilic colloid and wherein the polyhydroxy alcohol is present in the face coat in an amount within the range of 1 part by weight thereof to 10-20 parts by weight of the hydrophilic colloid.

7. A coated paper lithographic plate as claimed in claim 6 in which the hydrophilic colloid on the base sheet and in the face coat is selected from the group consisting of casein, alginates, carboxymethyl cellulose, polyacrylic acid, polyvinyl alcohol and starch.

8. A coated paper lithographic plate as claimed in claim 6 in which the polyhydroxy alcohol is selected from the group consisting of trimethylol propane, trimethylol ethane and trimethylol butane.

9. A coated paper which is stabilized against curling and puckering in response to exposure to elevated temperature and low humidity comprising a paper base sheet and a coating on the paper base sheet containing a hydrophilic colloid and a polyhydroxy compound of a lower hydrocarbon containing at least three primary hydroxyl groups in which the polyhydroxy compound is present in an amount within the range of 1 part by weight thereof to 1-20 parts by weight of the hydrophilic colloid.

10. A coated paper as claimed in claim 9 in which the polyhydroxy compound is present in the coating in an amount within the range of 1 part by weight thereof to 1-10 parts by weight of the hydrophilic colloid.

11. A coated paper as claimed in claim 9 in which the hydrophilic colloid is selected from the group consisting of casein, alginates, carboxymethyl cellulose, polyacrylic acid, polyvinyl alcohol and starch.

12. A coated paper as claimed in claim 9 in which the polyhydroxy compound is selected from the group consisting of trimethylol propane, trimethylol ethane and trimethylol butane.

13. A coated paper having plural coatings on one side comprising an outer coating containing a hydrophilic colloid as the binder and a polyhydroxy alcohol of a lower hydrocarbon containing at least three primary hydroxyl groups in an amount within the range of 1 part by weight of the polyhydroxy alcohol to 10-20 parts by weight of the hydrophilic colloid and an anchoring coat between the outer coating and the base sheet for anchoring the outer coating to the base sheet and containing a hydrophilic colloid as a binder and a polyhydroxy alcohol present in an amount within the range of 1 part by weight of the polyhydroxy alcohol to 1-10 parts by weight of the binder.

14. A coated paper as claimed in claim 13 in which the polyhydroxy alcohol is selected from the group consisting of trimethylol propane, trimethylol ethane and trimethylol butane.

15. A composition for use in the preparation of a coated paper lithographic plate comprising the combination of a hydrophilic colloid selected from the group consisting of casein, polyvinyl alcohol, starch, alginates, carboxymethyl cellulose and polyacrylates, a finely divided inert filler present in an amount within the range of 1 part by weight of the colloid to 1-8 parts by weight of the filler, an agent for insolubilization of the hydrophilic colloid and a polyhydroxy alcohol containing at least

three primary hydroxyl groups selected from the group consisting of trimethylol propane, trimethylol ethane and trimethylol butane present in an amount within the range of 1 part by weight of the polyhydroxy alcohol to 1-20 parts by weight of the hydrophilic colloid.

16. A coated lithographic paper plate comprising a paper base sheet having a insolubilized hydrophilic colloid coating on the base sheet containing an organic polyhydroxy alcohol containing at least three primary alcohol groups and selected from the group consisting of trimethylol propane, trimethylol ethane and trimethylol butane, and which is present in an amount within the range of

one part by weight of the polyhydroxy alcohol per 1-20 parts by weight of the hydrophilic colloid.

References Cited by the Examiner

UNITED STATES PATENTS

2,875,241	2/1959	Miller et al.	260-635
2,982,790	5/1961	Theiling et al.	260-635
3,135,808	6/1964	Robeson et al.	260-635

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