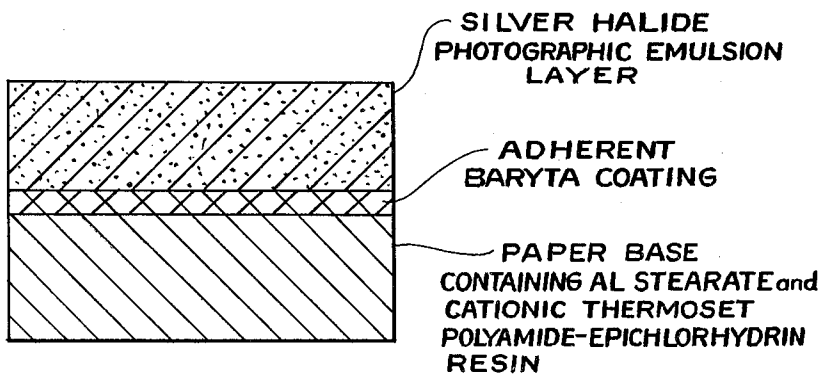


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METHOD OF MANUFACTURING PAPER FROM PARTIALLY
ESTERIFIED CELLULOSE FIBERS
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METHOD OF MANUFACTURING PAPER FROM PARTIALLY ESTERIFIED CELLULOSE FIBERS

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This invention relates to improving the wet strength and alcohol tolerance of paper prepared from partially esterified cellulose fibers.

Richter and Herdle application Serial No. 755,418, filed August 18, 1958, describes paper useful for photographic purposes, the fibers of which have lower fatty acid groups chemically combined therewith. Paper, the fibers of which have been partially esterified, is characterized by good stability and resistance to imbibition of aqueous salt solutions. It is desirable, however, to improve the wet strength of paper of this type. Often, however, materials regarded as useful for imparting good wet strength to ordinary paper are not effective to the same degree when employed in paper of partially esterified fibers. It is desirable that paper prepared from partially esterified fibers particularly for photographic purposes exhibit tolerance to coating solutions containing alcohol. Many materials which have been suggested for paper sizing do not impart this characteristic to partially esterified paper. In many cases, wet strength improvers in paper have rendered that paper brittle or otherwise altered the properties thereof so that increase in wet strength has been accomplished by the sacrifice of some other desirable property.

One object of our invention is to increase the wet strength of partially esterified paper by means especially adapted for use in paper composed of partially esterified fibers. Another object of our invention is to provide a paper which not only is characterized by superior wet strength but also exhibits tolerance to coating compositions containing alcohol. A further object of our invention is to provide a means for increasing the wet strength of partially esterified fiber paper which does not adversely affect other properties of the paper. A still further object of our invention is to provide a photographic paper base having highly desirable characteristics. Other objects of our invention will appear herein.

We have found that paper composed of partially esterified fibers is greatly improved in characteristics such as to render that paper valuable as a photographic paper base if there has been incorporated in that paper in its manufacture aluminum stearate or palmitate and a cationic thermosetting polyamide-epichlorohydrin resin of the type described in U.S. Patent No. 2,926,154. Paper, in accordance with our invention, is conveniently prepared by first beating partially esterified wood pulp fiber such as one having an apparent acetyl content of 20% to the desired slowness for papering-out use, thus forming a pulp slurry. To this slurry is first added an aqueous solution of sodium stearate. Efficient sizing is obtained if this is added at the rate of 0.45-4% fatty acid solids based on fiber weight. Instead of steric acid, some other fatty acid may be used such as palmitic acid. In making up this size, ammonium hydroxide might be employed rather than sodium hydroxide. After the sodium stearate has been thoroughly incorporated in the slurried fiber, there is added aluminum chloride or aluminum sulfate to precipitate the stearate size onto the fiber in the form of aluminum stearate (and stearic acid) and to reduce the pH to below 7 such as 6.0-6.5. This is conveniently accomplished in the mixing chest of the paper apparatus. If the water employed in diluting the slurry, such as white water, has a certain degree of alkalinity such

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that the pH would be raised above 7.0, it is desirable to reduce the pH below that figure by adding aluminum chloride or aluminum sulfate thereto.

There is then added to the slurry a solution of a cationic thermosetting polyamide-epichlorohydrin resin such as described in U.S. Patents No. 2,926,154 or 2,926,116 of Keim. This resin may be added to the slurry at any time prior to applying it to the wire of the paper machine preferably just prior thereto. This resin may be employed in a percentage within the range of 0.1-5% and desirably 0.5-3% based on the fiber, the range of 1-2% being optimum. It is desirable that the pH of the slurry be above 4.5 to obtain good curing of the thermosetting resin when in the paper. The slurry is applied to the wire of the paper machine in the convention manner and the paper formed is dried. It is desirable that the paper obtained be tub sized such as with a styrene-maleic acid or maleic anhydride type resin as described and claimed in application Serial No. 22,710 of ourselves and Alan Gray, filed of even date. The paper thus sized may also be conveniently subjected to a tub sizing with a gelatin solution. It has been found advantageous to include in this gelatin solution aluminum chloride or aluminum sulfate, this further treatment still further improving the alcohol penetration resistance of the paper. After the paper has been tub sized as desired, it is then subjected to a heat treatment such as by passing through an oven or by subjecting to infrared radiation as more fully described in application Serial No. 22,695 of ourselves and Alan Gray of even date. It is desirable to calender the paper with hot rolls.

The sodium stearate size which is used in preparing the paper in accordance with our invention is made up by mixing alkali and fatty acid together such as to form, for instance, the salt thereof usually sodium stearate. As an example, 62½ pounds of NaOH is dissolved in 1,250 gallons of water at 180-190° F. and 200 pounds of commercial stearic acid (29% palmitic, 69% stearic, 2% other fatty acid) is added thereto. The final solution contains 1.9% of fatty acid solids or 2.5% total solids. The NaOH is present in 114% excess in this solution. If desired, the NaOH used in preparing this size may be employed in stoichiometric amount or it may be present in smaller or larger excess than specified. The amount of alkali used is preferably sufficient to form a solution of all of the fatty acid employed. Ammonium hydroxide may be used as the alkali material, in which case it is ordinarily desirable to employ an excess of base. Instead of stearic acid, some other fatty acid such as lauric, myristic or the like may be employed.

The paper in accordance with our invention is prepared from fibers which are predominantly partially acylated such as having an apparent acetyl content of 15-25%. These fibers may have been acylated or some other lower fatty acid radical may have been imparted either as a portion of the acyl or instead of the acetyl. For instance, the cellulose fibers may have propionyl or butyryl groups chemically combined therewith providing the acyl content is within the range of 15-25%. The fibers of the paper prepared in accordance with our invention may be entirely partially esterified fibers or there may be some content of cellulose or other fibers therein. It is desirable, however, that the partially esterified fibers constitute 75-100% of the fiber content of the paper.

The accompanying drawing illustrating photographic paper in accordance with our invention shows in section the arrangement of layers therein in which the paper base is internally sized with aluminum salt of a higher fatty acid and cationic thermoset polyamide-epichlorohydrin resin. Applied to one face of the paper is a

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baryta coating over which is applied a silver halide photographic emulsion.

The following examples illustrate our invention:

Example 1

One pound of wood pulp acetylated to an acetyl content of 20% was beaten in a Valley beater to a Williams slowness of 30 seconds. A sample of the pulp slurry thus obtained was mixed with ½ cc. per gm. of pulp of a solution of sodium stearate containing 1.9% fatty acid solids. Following this, a 15% aqueous solution of aluminum chloride was added to bring the mass to a pH of 4.5. Ammonium hydroxide was then added to impart a pH of 8. This was followed by the addition of starch size and of a 2% solution of a cationic thermosetting polyamide-epichlorohydrin resin as described in Example 1 of U.S. Patent No. 2,926,154, this resin being added in the amount of 2% based on the weight of the fiber used. The slurry was then applied to a paper making screen and paper was prepared therefrom in the conventional manner.

For a control, one pound of wood pulp acetylated to an acetyl content of 20% was beaten in a Valley beater to a Williams slowness of 30 seconds and the following materials were added to a sample of the resulting pulp slurry with proper mixing between additions: 7% starch, ammonium hydroxide to a pH of 8.0, 2% of cationic thermosetting polyamide-epichlorohydrin resin and ½ % of stearoyl hexadecylethenone (alkyl ketene dimer). Paper was prepared from this slurry in the conventional manner. The papers prepared as described were run through a series of tests. Their properties compared as follows:

	A	Control
Elmendorf tear..... kg.	62	70
Perkins mullen..... p.s.i.	44	52
Wet tensile strength..... hectograms.	22	25
Penetration (Valley)..... sec.	2,000+	997
Expansion (2 min. in H ₂ O).....	0.60	0.90
Fold (M.I.T.).....	167	510
5 min. Cobb size (4% butyl alcohol) gms./100 cm. ²	0.386	(¹)

¹ Complete penetration.

Example 2

To 3,000 pounds of a slurry of wood pulp cellulose having an acetyl content of approximately 20% while in a chemical mixing chest was added 250 gallons of sodium stearate solution which had 1.33% fatty acid solids based upon fiber weight. Aluminum chloride was then added to the mass to reach a pH within the range of 6.0 to 6.5. To prevent the pH in the head box going above 7.0, aluminum chloride was added at that point in sufficient amount to maintain the pH adjustment following which there was added cationic thermosetting polyamide-epichlorohydrin resin in the form of its aqueous solution to supply 2% of resin based on the weight of the partially acylated fiber. The fiber slurry was applied to the wire of a paper machine in the conventional manner for making paper and the paper sheet thus obtained was calendered on hot rolls. The sheet thus prepared was tub sized with an aqueous solution of styrene-maleic anhydride resin and was then subjected to a temperature of 350° F. for 10 sec. to 2 minutes. A paper was obtained having good characteristics both as regards wet strength and resistance to any derogatory effect upon the application thereto of coatings containing butyl alcohol.

Example 3

Papers were prepared from partially acetylated fibers (acetyl about 20%) internally sized with aluminum stearate, stearic acid and cationic thermosetting polyamide-epichlorohydrin resin as described herein and surface sized with styrene-maleic anhydride resin and gelatin. Samples of these papers were baryta coated with a

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composition of 9.6–14.4 parts BaSO₄ and 1 part gelatin in 35–40% solids concentration in water-butyl alcohol (96:4). This coating may contain a gelatin hardener. The baryta coating was dried and super calendered. There was then applied thereover a gelatin-silver halide photographic emulsion layer. The emulsion employed may contain an alcohol therein without any adverse effect upon the paper base.

Other samples of the papers prepared as described were coated directly with gelatin-silver halide photographic emulsion layers. Emulsion compositions containing alcohol were found to have no adverse effect upon the paper base.

The papers thus obtained had excellent dimensional stability, were free of curl and could be processed in photographic processing solutions and dried at high rates without embrittlement or change in physical properties.

We claim:

1. A method of preparing paper which comprises forming an aqueous suspension of cellulose fibers the cellulose of which contains 15–25% of lower fatty acid groups chemically combined therewith adding to this suspension in that order a water soluble salt of a higher fatty acid, a water soluble aluminum salt of a strong mineral acid and a water soluble cationic thermosetting resin formed by reacting epichlorohydrin with a polyamide of C₃ to C₁₀, saturated aliphatic dibasic carboxylic acid and from about 0.8 to about 1.4 moles per mole of dibasic acid of a polyalkylene polyamine at a temperature from about 45° C. to about 100° C., said polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5–1 to about 1.8–1, adsorbing 0.1–5% approximately of said resin on said cellulose fibers, forming the cellulose fibers suspension into a sheet and heating the sheet to cure the resin to a water insoluble state.

2. A method of preparing paper which comprises forming an aqueous suspension of cellulose fibers the cellulose of which contains 15–25% of lower fatty acid groups chemically combined therewith, adding to the suspension in that order a water soluble salt of a higher fatty acid having a carbon content of 12–20 carbon atoms, a water soluble aluminum salt of a strong mineral acid and a water soluble cationic thermosetting resin formed by reacting epichlorohydrin with a polyamide of C₃ to C₁₀, saturated aliphatic dibasic carboxylic acid and from about 0.8 to about 1.4 moles per mole of dibasic acid of a polyalkylene polyamine at a temperature from about 45° C. to about 100° C., said polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5–1 to about 1.8–1, adsorbing 0.1–5% approximately of said resin on said cellulose fibers, forming the cellulose fibers suspension into a sheet and heating the sheet to cure the resin to a water insoluble state.

3. A method of preparing paper which comprises forming an aqueous suspension of cellulose fibers the cellulose of which contains 15–25% acetyl chemically combined therewith, adding to the suspension in that order, sodium stearate in aqueous solution, aluminum chloride in solution and a water soluble cationic thermosetting resin formed by reacting epichlorohydrin with a polyamide of a C₃ to C₁₀ saturated aliphatic dicarboxylic acid and from about 0.8 to about 1.4 moles per mole of dibasic acid of a polyalkylene polyamine at a temperature of from about 45° C. to about 100° C., said polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine being 0.5–1 to about 1.8–1, adsorbing about 0.1–5% approximately of said resin on said suspended pulp, forming the cellulose suspension into a sheet and heating the sheet to cure the resin to a water insoluble state.

4. A process according to claim 3 in which the alkylene polyamine is diethylene triamine.

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5. A process according to claim 4 in which the dicarboxylic acid is adipic acid.

6. Paper comprising sheeted fibers of cellulose which cellulose contains 15-25% of fatty acid groups of 2-4 carbon atoms chemically combined therewith containing an aluminum salt of a higher fatty acid of 12-20 carbon atoms and about 0.1-5%, based on the dry weight, of a cationic thermoset resin, said resin having been obtained by adding to said fibers of cellulose a water-soluble reaction product of epichlorohydrin, and a polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5-1 to about 1.8-1, said polyamide being obtained by heating together at a temperature from about 110° C. to about 250° C. a C₃ to C₁₀ saturated aliphatic dibasic carboxylic acid and from about 0.8 to about 1.4 moles per mole of dibasic acid of a polyalkylene polyamide, and curing said resin to a water-insoluble state by heating after said fibers have been formed into sheets.

7. Paper comprising sheeted fibers of cellulose which cellulose contains 15-25% of fatty acid groups of 2-4 carbon atoms chemically combined therewith, containing an aluminum salt of a higher fatty acid of 12-20 carbon atoms and about 0.1-5% based on its dry weight of a cationic thermoset polyamide-epichlorohydrin resin obtained by (1) reacting a C₃ to C₁₀ saturated aliphatic dibasic dicarboxylic acid with from about 0.8 to about 1.4 moles per mole of dibasic acid of a polyalkylene

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polyamine at a temperature from about 110° C. to about 150° C. to form a polyamide containing secondary amine groups and (2) reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 100° C. and at a ratio of epichlorohydrin to secondary amine groups of the polyamide to from about 0.5-1 to 1.8-1 to form a water-soluble cationic thermosetting resin which resin has been cured to a water-insoluble state by heating the paper after said fibers have been formed into sheets.

8. A paper product in accordance with claim 7 in which the aluminum salt of a higher fatty acid is aluminum stearate.

9. A paper product in accordance with claim 8 in which the dibasic carboxylic acid is a C₄ to C₈ saturated aliphatic dibasic carboxylic acid.

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