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SIZED PARTIALLY ESTERIFIED PAPER AND ITS METHOD OF PREPARATION

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This invention relates to partially esterified fiber paper sized with a modified polyvinylacetate latex size, its preparation and baryta coated photographic paper made therefrom.

It has been previously recognized that it is advantageous for paper of good dimensional stability that up to half of the hydroxyl of the cellulose fibers employed in its preparation be replaced by lower fatty acid radicals. Paper of this type as a base for photographic paper is described in application Serial No. 755,418 of George A. Richter and Lloyd E. Herdle. Many of the properties of paper are improved by tub sizing or surface sizing the paper. However, when partially esterified fiber paper is sized with commonly employed sizing materials a surface is obtained to which baryta coatings adhere poorly and which surface lacks in smoothness or other characteristics.

One object of our invention is to provide a surface size or tub size useful for sizing partially esterified fiber paper. Another object of our invention is to provide partially esterified fiber paper to which a baryta layer will adhere and which exhibits good smoothness under all normal conditions. A further object of our invention is to provide a partially esterified fiber paper having good water resistivity. A still further object of our invention is to provide a partially esterified fiber paper whose surface has been sized with a polyvinylacetate layer containing hydroxyethyl cellulose, plasticizer and Quilon chrome complex hardener. A still further object of our invention is to provide a photographic paper having good dimensional stability, improved physical strength, resistance to penetration by water, good surface properties and which is inert to photographically sensitive emulsions. Other objects of our invention will appear herein.

We have found that desirable characteristics are imparted to partially esterified fiber paper by surface sizing the paper with a modified polyvinylacetate latex which latex contains hydroxyethyl cellulose, plasticizer and Quilon chrome complex hardener. The partially esterified fiber paper is one in which 3–50% and desirably 8–40% of the hydroxyls of the cellulose fiber therein have been reacted with lower fatty acid radicals such as radicals of fatty acids of 2–4 carbon atoms. Paper of this type, which has been improved by internal sizing such as with cationic thermosetting polyamide-epichlorohydrin resin as described in U.S. Patents Nos. 2,926,154 and 2,926,116 of Keim and marketed by Hercules Powder Co. under the name Kymene is especially adapted to prepare a sized paper in accordance with our invention. Paper the fibers of which have been partially acetylated as described in Richter and Herdle application Serial No. 755,418 will be referred to herein as PA paper.

The tub sizing of PA paper in accordance with our invention may be conveniently performed by passing the paper after its formation and after drying through a bath of modified polyvinylacetate latex as will be described herein. The paper thus sized is preferably passed through squeeze rolls or other means to reduce the size content to 0.1–3 parts and preferably 2 parts (dry weight) of polyvinylacetate per 100 parts of cellulose. The paper is then dried such as by passing over heated rolls at a temperature of 125–150° F., preferably followed by calendering. Although higher temperatures up to 295° may be employed, it appears advantageous to dry the paper at lower temperatures as represented by the 125–150° F. range.

The composition of the modified polyvinylacetate latex used for tub sizing is composed of latex containing polyvinylacetate, plasticizer, hydroxyethyl cellulose and Quilon chrome complex hardener all dispersed in water. It is desirable that the water to polyvinylacetate ratio be 6–12:1. With too high a concentration of polyvinylacetate the latex may be too thick for good operations. It is desirable to have a small amount of hydroxyethyl cellulose present as a protective colloid in the latex such as 0.5–5% of hydroxyethyl cellulose based on the weight of the polyvinylacetate. The presence of a plasticizer compatible with the latex is desirable. The concentration of plasticizer is not critical but 3–35% thereof desirably 5–25% and preferably about 10% based on the polyvinylacetate can be conveniently used. The use of plasticizer in minimum proportion contributes to good surface smoothness of the paper and avoids roughness upon rewetting. The plasticizers which have been found to be particularly useful are the aliphatic esters of dicarboxylic acids such as the phthalates, adipates and the sebacates. Some plasticizers of this type are dibutyl phthalate, dibutyl sebacate, methoxyethyl phthalate, dibutyl adipate, di-2 ethylhexyl phthalate, dioctyl sebacate, and the like. However, plasticizers illustrated by the butyl ether of diethylene glycol acetate are particularly useful in this connection. Quilon chrome complex is added in small proportion such as 1–10% based on the weight of the polyvinyl acetate. Quilon, which is a product marketed by the Du Pont Company, is a water soluble Werner type chromium complex (whose preparation is described in U.S. Patent 2,273,040 of Iler) dissolved in an aliphatic alcohol (isopropanol). This complex may be a stearic acid complex or a myristic acid complex or the complex of chromium oxychloride with some other fatty acid of at least 10 carbon atoms.

Paper tub sized as described herein is useful as the base for photographic paper. For instance the paper so prepared may be baryta coated such as by applying thereto a coating of barium sulfate in an aqueous solution of gelatin in the conventional manner whereupon a gelatin-silver halide photographic emulsion layer may be applied thereover.

It appears that particularly good paper properties are obtained in sizing paper in accordance with our invention if the paper after applying the size thereto is first subjected to drying at a low temperature such as about 125° F. followed by raising the temperature to complete moisture removal from the paper.

The following examples illustrate our invention:

Example 1

Paper of 31 lbs. basis weight (31 lbs. per 1000 sq. ft.) made from kraft fiber which had been partially acetylated to approximately 21% acetyl content and internally sized with a cationic thermosetting polyamide-epichlorohydrin resin (such as that marketed by Hercules Powder Company under the trade name Kymene 557) was tub sized by passing through a sizing bath as described below for 5 seconds at 70° F. and dried for 4 minutes at 125° F. The sized paper was supercalendered using 4 nips at 140° F. and 30 p.s.i. pressure. The composition sizing of the sizing bath was (parts being by weight): 100 parts of polyvinylacetate latex (e.g. Carbide and Carbon latex WC 130 or Shawinigan latex Gelva TS–70 containing 58.8% solids which includes a small proportion of hydroxyethyl cellulose) 5.9 parts of dibutylphthalate, 10 parts of Quilon M (myristo chromic chloride, 30% solids in isopropyl alcohol) and 400 parts of water. The sizing bath

had been prepared by adding the dibutylphthalate to the latex, allowing to stand for 24 hours, and then diluting with water and Quilon. The properties of the sheet so prepared were compared with a sheet prepared in the same manner except that no surface sizing was used. Tests showed that the sized paper had substantially the same properties as the unsized paper except that it was resistant to water penetration whereas the unsized paper was completely penetrated. The test results were as follows:

	Sheet Properties	
	Sized	Not sized
Tear:		
L	98	94
C	106	99
Mullen	53	43
Wet Tensile Strength	32	28
Penetration (sec.)	2,000+	2,000+
Expansion	1.40	1.65
Folds:		
L (flexibility)	72	75
C (flexibility)	65	99
Cobb size (g./100 cm.²) (4% BuOH)	.17	[1] CP

[1] CP=complete penetration

Example 2

The above procedure was repeated except that paper of 27 lbs. basis weight was used and the sizings employed were not only as described in Example 1 but on various other samples of the paper polyvinylacetate latex (without Quilon and plasticizer), gelatin, acrylic latex, styrene butadiene latex, polystyrene latex or no latex at all were respectively applied. The results obtained were as follows:

Surface Size	Paper of 19–21% acetyl content and internally sized with Kymene					
	Cobb Size			Measure of Baryta Surface		
	H_2O	BuOH[1]	Dektol	Uncal.	Cal.	Wet and Redry
Gelatin	0.140	0.259	0.402	8.4	9.6	5.8
PVAc	0.157	0.262	0.518	8.8	8.2	8.4
PVAc+Q+DBP	0.108	0.132	0.113	0.7	3.1	5.4
Acrylic latex	Complete Penetration					
Styrene-butadiene latex.	Partial Penetration					
Polystyrene latex	Complete Penetration					
None	0.157	0.278	com. pen.			

[1] Butyl alcohol—4% in water.

The mixture of polyvinylacetate, Quilon and plasticizer offered substantial advantage in resistance to penetration of water, butyl alcohol solution and Dektol photographic developer solution. Because of improved resistance to water and butyl alcohol a baryta coated surface on this paper is smoother than that obtained using other sizing materials. The resistance to water and Dektol developer also contributes to faster photographic processing and drying.

The Cobb size test measures the effectiveness of the sizing of a sheet of paper. Essentially a liquid is permitted to remain in contact with 100 cm.² of surface area of the paper for an interval of time. The excess liquid is blotted off and the gain in weight is measured. The gain in weight in grams/100 cm.² is the Cobb size value. The time of contact was 2 min. for the water and the Dektol developer (1:1 in water); for the butyl alcohol (4% in water) the contact time was 5 min.

The baryta surface measurements were made on a Surfanalyzer. This instrument measures the shadow pattern cast by the surface when illuminated by a light 4° from the horizontal. The values are relative within a given frequency range and sensitivity setting. For the non-calendered paper ("uncal." in the table) and the super-calendered paper wet for 20 min. and dried ("wet and redry" in the table) the frequency setting was 0–2000 c.p.s. with a sensitivity setting of 775 and a frequency setting of 200–2000 c.p.s. with a sensitivity setting of 795, respectively. At these settings an uncalendered surface with a Surfanalyzer reading of 0.7 would be considerably smoother than an uncalendered surface with a reading of 8.4 but would be rougher than a calendered surface with a reading of 8.4 because of the greater sensitivity of measurement for the calendered surface.

We claim:

1. Paper, 3–50% of the hydroxyl of the cellulose fibers of which has been replaced by lower fatty acid radicals, which paper has a polyvinyl acetate surface sizing which contains hydroxyethyl cellulose, plasticizer and water-soluble Werner type chromium complex in which a trivalent nuclear chromium atom is co-ordinated with an acyclic carboxylic acid group having at least 10 carbon atoms.

2. Paper, 3–50% of the hydroxyl of the cellulose fibers of which has been replaced by lower fatty acid radicals, internally sized with a cationic polyamide-epichlorohydrin resin, which paper has a polyvinyl acetate surface sizing which contains hydroxyethyl cellulose, plasticizer, and water soluble Werner type chromium complex in which a trivalent nuclear chromium atom is co-ordinated with an acyclic carboxylic acid group having at least 10 carbon atoms.

3. Paper, 3–50% of the hydroxyl of the cellulose fibers of which has been replaced by acetyl, which paper has a polyvinyl acetate surface sizing which contains hydroxyethyl cellulose and water soluble Werner type chromium complex in which a trivalent nuclear chromium atom is co-ordinated with an acyclic carboxylic acid group having at least 10 carbon atoms.

4. Paper, 3–50% of the hydroxyl of the cellulose fibers of which has been replaced by lower fatty acid radicals, which paper has a polyvinyl acetate surface sizing which contains hydroxyethyl cellulose, plasticizer and water-soluble Werner type chromium complex in which a trivalent nuclear chromium atom is co-ordinated with an acyclic carboxylic acid group having at least 10 carbon atoms, and a coating thereon of barium sulfate and gelatin.

5. A method of preparing paper useful for photographic purposes which comprises surface sizing paper, 3–50% of the hydroxyl of the cellulose fibers of which have been replaced by lower fatty acid radicals, with an aqueous solution of polyvinyl acetate containing hydroxyethyl cellulose, plasticizer, and a water-soluble Werner type chromium complex in which a trivalent nuclear chromium atom is co-ordinated with an acyclic carboxylic acid group having at least 10 carbon atoms followed by drying of the paper by means of heated rolls.

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