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METHOD OF IMPROVING THE STRENGTH CHARACTERISTICS OF PAPER PREPARED FROM PARTIALLY ACYLATED CELLULOSE FIBERS

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This invention relates to the manufacture of paper composed of partially esterified cellulose fibers improved in strength characteristics by sizing with styrene-maleic acid or styrene-maleic anhydride type resins having therewith a cross-linking agent and subsequently heat treating at a temperature within the range of 350–400° F. such as with infrared heat or oven for a time short of that which would cause discoloration of the paper.

Paper as ordinarily prepared is useful for numerous purposes such as wrapping, writing paper, newsprint, printing paper, and many other of the common uses for that material. Paper has also been found to be useful for special purposes but modifications in the usual paper making processes to prepare paper for those specialy purposes are sometimes necessary. For instance, it is desirable that paper for photographic purposes exhibit good stability and resistance to imbibition of salts in processing operations. Papers subjected to aqueous baths have often been characterized by curling. This is particularly objectionable in photographic processing and in the finished photographic products.

The application of a waterproof coating to paper for photographic purposes such as the application of a cellulose ester coating thereto has been suggested. Oftentime waterproof paper exhibits a certain amount of stiffness and in many cases offers resistance to the application of a coating of an aqueous photographic emulsion thereon. The cost of preparing waterproofed paper for photographic purposes has often been high which has precluded its use in commercial manufacture.

It has been discovered in recent years that paper comprising cellulose fibers chemically combined with lower fatty radicals exhibits properties superior to those of paper prepared from conventional wood pulp fibers. For instance, paper prepared from cellulose fibers having a lower fatty acid radical content of 15–25%, apparent acetyl, exhibits good dimensional stability and freedom from appreciable curl. Also, paper of this type is characterized by low water and salt retention in photographic processing operations in comparison with many types of paper base which have been employed heretofore. It is desirable in the case of paper prepared from partially acylated fibers that it in addition exhibit high strength and good resistance to certain coating solvents. It is also desirable that such a paper be resistant to size change when subjected to atmosphere varying in relative humidity or to the aqueous baths used in photographic processing.

One object of our invention is to provide a method for treating paper of partially acylated fibers involving the use of heat whereby the strength of that paper is increased. Another object of our invention is to provide a method for treating paper of partially acylated fibers in which its resistance to the effects of certain coating solvents is enhanced. A further object of our invention is to provide a method for treating paper in which the dimensional stability properties as represented by changes during wetting are enhanced. A still further object of our invention is to prepare a partially acylated paper compatible with silver halide photographic emulsions. Other objects of our invention will appear herein.

The partially acylated paper treated in accordance with our invention is composed of 75–100% of partially acylated cellulose fiber, the cellulose fibers being chemically combined with fatty acid radicals of 2–4 carbon atoms which fibers then have a combined apparent acetyl content of 15–25%. In making the paper, the acylated fiber is conveniently dispersed in water to form an aqueous slurry and beaten to a slowness useful for the paper making operations. If any other fiber is used, it is present in an amount no more than 25% of the total fibers of the paper. This other fiber may be a wood pulp or a rag fiber as commonly used to make paper of sheet quality. After beating, the pulp slurry is applied to the wire of a paper machine preferably after first incorporating sizing therein such as described in Griggs and Zaffrann application Serial No. 22,711, filed on even date. After the paper is formed and desirably after drying, it may be tub sized with a styrene-maleic anhydride or styrene-maleic acid resin preferably after this resin has been mixed with a non-formaldehyde cross-linking agent such as a diepoxide resin. The paper is then subjected to a heat treatment such as that obtained by bringing the paper to a temperature of 350–400° F., preferably 350–375° F., for a period of at least 5 and preferably 10 seconds but short of causing discoloration of the paper.

The method of sizing paper with the styrene resin materials is described in application Serial No. 22,710 of ourselves, filed of even date.

In accordance with our invention, the paper is subjected to the 350–400° F. temperature for a short time so as to avoid discoloration as may occur with prolonged heating. When the heating operation is carried out in an oven, the operation can be from 5 seconds up to 2 minutes or possibly longer without discoloration occuring. When heating by infrared rays is used, the paper is heated up so much faster that the time of heating should ordinarily be limited to less than a minute to avoid discoloration. If the heating is carried out by passing the paper between rolls heated to 350–400° F., the time of contact is ordinarily sufficiently short that discoloration is avoided.

We have found that by sizing partially acylated fiber paper and heat treating in accordance with our invention, substantial increases of mullen and wet tensile strength are obtained and resistance to water penetration is somewhat better than with paper prepared from partially acylated cellulose fibers without the described sizing and heat treatment. In addition, there is a substantial improvement in the dimensional stability as indicated by the decrease in the wet expansion.

If paper is formed in the manner described above but sized with a gelatin solution in preference to the styrene-maleic anhydride or acid resin solution, similar results may be realized but to a less extent than with styrene-maleic anhydride resin sized paper.

The following examples illustrate the preparation of paper both with and without the utilization of our invention and a comparison of the characteristics obtained:

EXAMPLE 1

A roll of paper was prepared from cellulose fibers having a combined acetyl content of approximately 20% which had been internally sized with 7% starch, 2% of a cationic thermosetting polyamide-epichlorohydrin resin, as described in Example 1 of U.S. Patent No. 2,926,154, and ⅛% of stearoyl hexadecylethenone (alkyl ketene dimer), all based on the weight of the fiber, dyes also having been added, in a manner similar to that described in Griggs and Zaffrann application Serial No. 786,041, filed January 12, 1959. Half of this roll of paper was sized with 2% gelatin aqueous solution. The other half of the roll of paper was also sized with a 2% gelatin solution but then was subjected to an infrared

heat treatment in such a manner that the sheet temperature came to 350° F. in about 5 seconds and remained at about 350–375° F. for another 5–10 seconds. The papers were both tested with the results given in columns A and B of Table I which follows. It is to be noted that there was an increase of approximately 20% in wet tensile strength, a substantial increase in penetration resistance and a reduction in expansion, swell and bulk and in Cobb size of the infrared treated paper (B) compared with the paper not subjected to 350° F. temperature.

EXAMPLE 2

A roll of paper was prepared from partially acetylated fibers in a manner similar to that described in the preceding example except that the paper was sized with a mixture of 2% each of styrene-maleic anhydride and styrene-maleic acid resins as described in application Serial No. 22,710 of ourselves, filed of even date. This roll of paper was water finished and one half was treated with infrared rays in such a manner that the sheet temperature came to about 350° F. in about 5 seconds and remained at 350–375° F. for another 5–10 seconds. Columns C and D of the table are the results obtained when testing the paper not subjected to 350° F. temperature (C) and that subjected to infrared heat (D). It will be noted that in the case of the infrared heated paper as compared with the paper not subjected to high temperature, there was a 16% increase in wet tensile strength, a marked improvement in dimensional stability as measured by reduction in expansion, swell and bulk and improved resistance to solvent effect as measured by decrease in Cobb size value.

EXAMPLE 3

A roll of paper was prepared from partially acetylated fibers in the manner described in Example 1. The paper was water finished and one half of the roll was heat treated in an oven at 350° F. for 2 minutes. The results are given in columns A (not heat treated) and E (heat treated) in the following table. It will be noted that there was a 25% increase in Mullen, a 33% increase in wet tensile strength, a substantial increase in penetration and a marked improvement in dimensional stability as measured by a reduction in expansion, swell and bulk of the heated treated paper (E) over that which had been given no heat treatment (A).

EXAMPLE 4

A roll of paper was prepared from partially acetylated fibers in the manner described in Example 2. This roll of paper was water finished and one half was passed through an oven wherein it was subjected to a treatment at 350° F. The results are given in column C (not heat treated) and column F (heat treated) in the following table. It will be noted that there is a 50% increase in wet tensile strength and a marked improvement in dimensional stability as indicated by the reduction in expansion, swell and bulk of the heat treated paper (F) over that which had been given no heat treatment (C).

Table I

	A	B	C	D	E	F
Weight	22¾	20¾	23½	24	22¾	23½
Thick. (dry	4.3	4.2	4.7	4.9	4.3	4.7
Tear:						
L	81	72	84	82		
C	86	74	87	90		
Mullen	27	27	36	37	34	38
Wet Tensile Str	23	28	30	35	31	46
Penetration	514	2,000+	2,000+	2,000+	2,000+	2,000+
Expansion	1.55	1.30	1.80	1.10	1.20	0.95
Fold:						
L	69	76	84	145	147	116
C	56	110	70	171	121	129
Percent Swell	39	19	32	22	25	21
Percent Bulk	15	2	8.5	4	8	2
Cobb Size	0.16	0.140	0.144	0.092	0.19	0.10

The swell and bulk values are obtained from the following formulas after determining the dry thickness of the paper by soaking the paper for 20 minutes in water at room temperature and in the case of the former, determining the wet thickness and in the case of the latter, the thickness upon redrying the paper to about 5% moisture content.

$$\text{Percent swell} = \frac{\text{Wet thick} - \text{dry thick}}{\text{Dry thick}} \times 100$$

$$\text{Percent bulk} = \frac{\text{Wet, redried thick} - \text{dry thick}}{\text{Dry thick}} \times 100$$

EXAMPLE 5

Samples of partially acetylated paper which had been internally sized with aluminum stearate and cationic thermosetting polyamide epichlorohydrin resin as described in Griggs and Zaffrann application Serial No. 22,711, filed of even date, were surface sized with gelatin as described in Example 1 or with styrene-maleic anhydride resin sizing as described in Example 2 and were subjected to an infrared heat treatment in such a manner that the sheet temperature came to about 350° F. in about 5 seconds and remained at about 350–375° F. for another 5–10 seconds. These papers exhibited characteristics superior to those of like paper which had been surface sized with gelatin or with styrene-maleic anhydride resin but which had not been subjected to the heat treatment.

The paper prepared as described in accordance with our invention is eminently useful either with or without a baryta ($BaSO_4$+gelatin) coating as a support for gelatino-silver halide photographic emulsions. In those cases where the emulsion layers are unhardened, it is desirable to omit the gelatin size coating of the paper, the emulsion then being applied directly to the styrene-maleic resin size layer with or without a preliminary baryta coating.

We claim:

1. A method of manufacturing paper of good strength characteristics which comprises preparing paper of fibers at least 75% of which are cellulose fibers having an acyl content of 15–25%, apparent acetyl, surface sizing the thus prepared paper and subsequently subjecting the paper to a temperature within the range of 350–400° F. for a time short of that which will cause discoloration of the paper.

2. A method for the manufacture of paper having good strength characteristics which comprises preparing a paper from cellulose fibers at least 75% of which are cellulose having an acyl content of 15–25%, apparent acetyl, surface sizing the paper with a styrene-maleic resin and subjecting the thus sized paper to a heat within the range of 350–400° F. for a time short of that which will cause discoloration of the paper.

3. A method of manufacturing paper having good strength characteristics which comprises preparing paper from cellulose fibers at least 75% of which are cellulose having an acyl content of 15–25%, apparent acetyl, surface sizing the paper with gelatin and subjecting the thus sized paper to a temperature within the range of 350–400° F. for a time short of that which will cause discoloration of the paper.

4. A method of preparing paper having good strength characteristics which comprises preparing paper from cellulose fibers at least 75% of which have been cellulose having an acyl content of 15–25%, apparent acetyl, surface sizing the paper with a sizing material selected from the group consisting of gelatin and styrene-maleic resin and subsequently subjecting the thus sized paper to treatment with infrared rays sufficient to heat the paper to a temperature within the range of 350–400° F. for a time short of that which would cause discoloration of the paper.

5. A method of [illegible]

fibers at least 75% of which have been cellulose having an acyl content of 15–25%, apparent acetyl, surface sizing the thus formed paper with a sizing material selected from the group consisting of gelatin and styrene-maleic resin and subsequently treating the paper in an oven at a temperature within the range of 350–400° F. for a time short of that which will cause discoloration of the paper.

6. In the preparation of paper, in which paper, prepared from cellulose fibers having an acyl content of 15–25%, apparent acetyl, and internally sized with a cationic thermosetting polyamide-epichlorohydrin resin, is surface sized with a sizing selected from the group consisting of gelatin and styrene-maleic resin, the subsequent step which comprises subjecting the paper to a temperature within the range of 350–400° F. for a time short of that which causes discoloration of the paper.

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