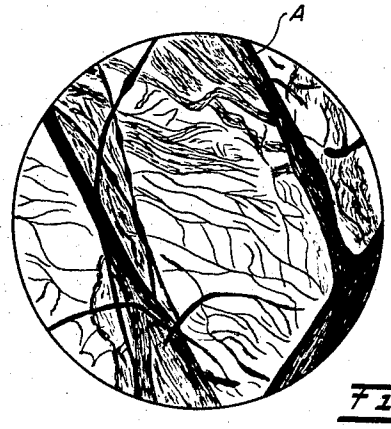
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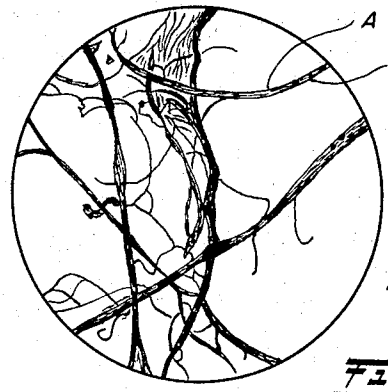
METHOD OF SIZING PAPER WITH CATIONIC POLYAMINE AND CARBOXYLIC ANHYDRIDE

Filed Oct. 28, 1966



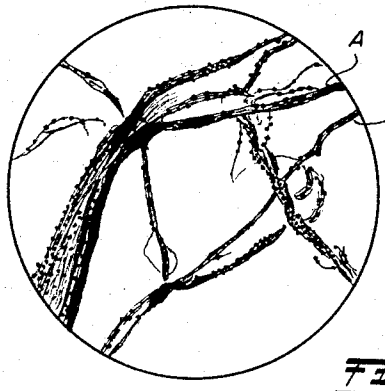
25,000X

Fig. 1



25,000X

Fig. 2



25,000X

Fig. 3

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United States Patent Office 3,409,500 Patented Nov. 5, 1968

3,409,500

METHOD OF SIZING PAPER WITH CATIONIC POLYAMINE AND CARBOXYLIC ANHYDRIDE

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Continuation-in-part of applications Ser. No. 112,959, May 26, 1961; Ser. No. 423,895, Dec. 23, 1964; and Ser. No. 490,617, Sept. 27, 1965. This application Oct. 28, 1966, Ser. No. 598,576

10 Claims. (Cl. 162—164)

ABSTRACT OF THE DISCLOSURE

Sized paper is manufactured by separately adding an aqueous anionic dispersion of hydrophobic organic cellulose-reactive paper sizing carboxylic anhydride particles to an aqueous suspension of cellulose paper-making fibers and a water-soluble cellulose-substantive cationic polyamine having a molecular weight in excess of 1,000, sheeting said suspension to form a water-laid web, and drying said web at a temperature between 190° F. and 250° F. The amount of polyamine added is sufficient to deposit the carboxylic anhydride particles on the fibers and to accelerate the rate at which the anhydride develops its sizing properties when the web is dried.

This is a continuation-in-part of our copending applications Ser. Nos. 112,959, 423,895, and 490,617 respectively filed on May 26, 1961, Dec. 23, 1964, and Sept. 27, 1965, and now all abandoned.

The present invention relates to the manufacture of sized paper by use of anionic dispersions of organic paper-sizing carboxylic anhydrides in conjunction with water-soluble cellulose-substantive cationic polymers.

Nathansohn U.S. Patent No. 1,996,707 (1935) discloses that well-sized paper is obtained when an anionic dispersion of a hydrophobic organic acid anhydride [for example, distearic acid anhydride,

$$CH_3(CH_2)_{16}CO—O—OC—(CH_2)_{16}CH_3]$$

is added to papermaking cellulose pulp during the papermaking operation.

However, the process has not achieved commercial success, most probably because the paper must be heated 3 to 6 hours at 80° C. to 110° C. to cause the anhydride to develop its sizing properties. Present-day commercial practice requires that the ultimate sizing of paper develop more rapidly, and it is generally preferred that the sizing develop fully while the paper is in the papermaking machine, i.e., before it is formed into rolls.

Present-day machine schedules generally complete the drying step in ⅛ to 3 minutes in the temperature range mentioned.

More rapid development of sizing is disclosed by British Patent No. 804,504 (1958) which employs as beater additive a dispersion of stearic anhydride and bentonite. The dispersion is anionic, no cationic material is employed, and the process has evidently not proved satisfactory for commercial use.

The discovery has now been made that anionic dispersions of hydrophobic acid anhydrides rapidly develop their sizing properties in the manufacture of sized paper when they are employed in conjunction with a separately-added, water-soluble, cellulose-substantive, cationic polyamine. In preferred instances, we have obtained nearly all of the ultimate sizing in three minutes at 250° F. (equivalent to machine drying), and the numerical sizing values obtained have been very high. This increase in speed results from the fact that the polyamine acts as a catalyst or promotor for the anhydride-cellulose reaction,

and is not the consequence of more uniform deposition of the anhydride particles on the fibers.

In the drawing:

FIGURE 1 shows untreated cellulose paper-making fibers;

FIGURE 2 shows cellulose papermaking fibers which have been treated in aqueous suspension by addition of an aqueous dispersion containing 0.4% of their dry weight of a distearic anhydride dispersion prepared by emulsifying molten distearic anhydride at 80° C. with the aid of potassium stearate as emulsifying agent, after which the fibers were washed with distilled water, resuspended in distilled water and formed into a sheet; and

FIGURE 3 shows fibers which have been treated as shown in FIGURE 2 except that 0.2% based on the dry weight of the fibers, of a water-soluble cationic tetraethylenephentamine - epichlorohydrin resin was added after the dispersion, then washed with water to remove all unbound particles and sheeted.

In FIGURE 1, the fibers carry substantially no foreign matter and possess no sizing.

In FIGURE 2, the fibers carry mechanically entrapped particles of distearic anhydride. These particles, however, are irregularly located and are few in number, and the paper possesses practically no sizing.

In FIGURE 3, the fibers carry a very large number of distearic anhydride particles. The particles are uniformly distributed over the fibers and the fibers are very well sized after completion of machine drying.

In the figures, A designates the cellulose fibers and B designates distearic anhydride particles.

The process of the present invention may be performed by adding an aqueous anionic dispersion of hydrophobic organic cellulose-reactive paper sizing anhydride particles to an aqueous suspension of cellulose papermaking fibers, separately adding to the suspension a water-soluble cellulose-substantive cationic polyamine, sheeting the suspension to form a water-laid web, and drying the web at a temperature between 190° F. and 250° F.

Slightly better sizing values have generally been obtained when the cationic polyamine is added subsequently to the anionic sizing emulsion. Thus it is generally best to add the sizing dispersion in the beater or stock chest and to add the cationic agent near the wire, for example at the head box.

The pH of the fibrous suspension on and after addition of the treating agents is not critical. Our present evidence is that best sizing generally develops when the pH of the suspension, after treatment, is in the range of pH 5 to 8.

The invention does not depend upon which hydrophobic anhydride or mixture of anhydrides is used. Suitable anhydrides are disclosed in the Nathansohn patent cited above and in British Patents Nos. 451,300 and 804,504. They are water-insoluble water-repellent carboxylic anhydrides which esterify with cellulose when heated therewith.

A sufficient amount of polyamine is that which deposits an effective amount for sizing purposes of the anhydride particles on the fibers. This amount of polyamine is sufficient to accelerate the rate at which the anhydride develops its sizing when heated at 190° F.–250° F. and to produce a perceptible catalytic effect.

Small amounts of the polyamine cause a perceptible amount of catalysis, and larger amounts cause a more pronounced catalytic effect, in preferred instances more than 90% of the ultimate sizing being achieved in 3 minutes of drying at 212° F.–250° F. The amount varies from instance to instance depending chiefly on the cationic strength of the cationic compound used, its molecular weight, and the pH of the suspension, and in any one instance is conveniently found by laboratory trial. Gener-

ally there is an optimum amount of polyamine, and larger amounts are often less effective than smaller amounts. Preferably sufficient of the polyamine (or mixture of polyamines) should be added to decrease the negative charge of the fibers (the electrokinetic or "zeta" potential of the fibers) to about zero; this amount can readily be determined in any instance by use of an electrophoresis cell.

Suitable cationic compounds are water-soluble primary, secondary, tertiary and quaternary polyamines which, when added to an aqueous suspension of cellulose fibers, render the fibers positively charged, as shown by the behaviour of the fibers in an electrophoresis cell.

Monomeric amines and polyamines including tetraethylenepentamine cause little if any catalysis. Their use is consequently outside of the scope of the present invention.

Suitable cationic polyamines include polyethylenimine and other water-soluble linear polymers having a substantial proportion of $-CH_2CH_2NH-$ linkages; water-soluble cationic starch; polyvinylamine; polymeric tertiary amines for example polyvinylpyridine; poly N-methyl pyridinium chloride; the methylamine-ammonia-epichlorohydrin condensation product (and similar products) of Coscia U.S. Patent No. 3,248,353; urea-formaldehyde-polyalkylene polyamine wet strength resins for paper such as are disclosed in Suen et al. U.S. Patent No. 2,554,475 (1951) and Jen et al. U.S. Patent No. 2,885,318 (1959); the 50:2 molar ratio acrylamide:diallyldimethylammonium chloride copolymer, casein, glue and water-soluble vinyl polymers rendered cationic by reaction with alum. The last-mentioned group of agents are prepared by adding alum to an aqueous solution of the casein, glue or polymer; the reaction proceeds rapidly. Polyamides which contain no amino groups such as the cationic resin of U.S. Patent No. 2,345,543 possess little, if any, catalytic activity and hence are outside of the scope of the present invention. In general, the more highly cationic the polymer (i.e., the more amino groups which each polymeric macromolecule contains), the more catalysis it produces.

The cationic starch referred to above is water-soluble starch carrying sufficient cationic amino, quaternary ammonium or other cationic groups to render the starch as a whole cellulose-substantive.

Cationic polyamines having a molecular weight in excess of 1,000 are preferred because in general they are more effective per unit weight and because they are benefitted by the presence of alum (up to about 5% of the dry weight of the fibers), which thus acts as a fortifying agent or extender, often permitting a substantial reduction in the amount of cationic agent needed to achieve a given level of sizing or improving the sizing which would otherwise result. The alum may be added before, with or after the cationic polymer. The effect of alum is most apparent when the amount of cationic polymer is comparatively small. Moreover, it is preferred that the polymer contain at least one amino group (primary, secondary, tertiary or quaternary ammonium) for every 10 carbon atoms therein, so that the polymer possesses strong cationic properties.

Among the most efficient cationic polymers are the adipic acid-polyalkylenepolyamine-epichlorohydrin polymers, prepared by condensing adipic acid with a polyalkylene-polyamine thereby forming a polyamidepolyamine, and reacting this polymer with epichlorohydrin. Methods for the preparation of agents of this type are disclosed in Keim U.S. Patents Nos. 2,926,116 and 2,926,154 and in copending application Ser. No. 281,321, filed on May 17, 1963, now U.S. Patent No. 3,329,657, by myself and Ronald R. House.

The organic paper-sizing acid anhydrides generally have melting points lower than 95° C. and can therefore be emulsified in hot water containing an appropriate anionic emulsifier.

It is usually advantageous to pass the emulsion through a homogenizer to decrease the dimensions of the emulsified droplets as much as practical, after which the emulsion is immediately and rapidly cooled to form a solid-in-liquid dispersion. The emulsion is a microscopically heterogeneous mixture of the paper sizing acid anhydride droplets in a continuous aqueous phase. The droplets are predominantly below 1μ in diameter and our experience is that the finer the droplets, the more efficient are the sizing results. The rapid cooling converts the liquid droplets to solid particles without substantial change in dimensions.

The solids content of the sizing dispersions as prepared is a matter of convenience. The dispersions are advantageously diluted to ½%–5% solids before use to ensure uniform distribution of the size through the paper pulp.

The invention is further illustrated by the examples, which constitute specific embodiments of the invention and which are not to be construed in limitation thereof.

EXAMPLE 1

The following illustrates the manufacture of sized paper according to the invention showing the variety of cationic agents that may be employed.

An anionic emulsion of a hydrophobic organic paper sizing anhydride is prepared by slowly pouring 60 g. of molten distearic anhydride with vigorous agitation into 930 cc. of vigorously agitated water containing 6 g. of dissolved gum ghatti and 3 g. of the anionic emulsifying agent formed by reacting one mol of naphthalene sulfonic acid with two mols of formaldehyde. A creamy emulsion forms which is homogenized hot and is then rapidly cooled to prevent coalescence of the dispersed phase.

Samples of sized paper are prepared by forming an aqueous suspension of well-beaten 50% bleached sulfite–50% hardwood pulp at 0.6% consistency, dividing the pulp into aliquots, adding amounts of the above emulsion and the cationic agent [tetraethylenepentamine-epichlorohydrin resin of Example 1 of Daniel et al. U.S. Patent No. 2,595,935 (1952)] shown in the table below, the cationic agent being added after the anionic emulsion, stirring the suspensions for about a minute after each addition, and forming handsheets from the pulp samples at a basis weight of 100 lbs. per 25" x 40"/500 ream, according to standard laboratory procedure.

The handsheets are dried for three minutes on a rotary laboratory drum drier at 250° F. (two passes of 1.5 minutes each), and the lactic acid resistance of the sheets is determined by penescope using a 20% lactic acid solution at 100° F. under a 12" head, after which the sheets are cured at 220° F. for one hour to develop substantially their ultimate sizing.

Results are as follows:

Run No.	Percent Anionic Emul. Added [1]	Percent Cationic Agent Added [1]	Sizing Developed, Secs.		Percent Ultimate Sizing Developed In 3 mins.
			250° F.,[2] 3 mins.	220° F.,[2] 1 hour	
1	0.1	0.1	Inst.		
2	0.2	0.1	>3,900	>3,900	
3	0.3	0.1	>3,900	>3,900	
4	0.2	0.05	3,000	3,200	94
5	0.2	0.1	>3,900	>3,900	
6	0.2	0.3	>3,900	>3,900	
7	0.2	0.6	2,040	2,560	80

[1] Solids based on dry weight of fibers.
[2] Temperature of drum of drier.

From other laboratory work, it is known that similar results are obtained when the cationic agent is added before the anionic agent.

EXAMPLE 2

The following illustrates the manufacture of sized paper according to the present invention showing a number of the cationic compounds which can be used.

The procedure of Example 1 is repeated except that the tetraethylenepentamine-epichlorohydrin resin is replaced by the resins shown in the table below. When used,

the alum is added after the sizing agent and polymer. The sheets are made at a basis weight of 100 lbs. per 25" x 40"/500 ream, and are dried for three minutes on a laboratory drum drier having a drum temperature of 250° F.

No.	Percent Anionic Emul. Added [1]	Catonic Agent		Lactic Acid Resist. After Drying for 3 Mins. at 250° F.[7]
		Name	Percent Added [1]	
1	0.3	None (Control)	None	Inst.
2	0.3	Polyethylenimine	0.03	1,800.
3	0.3	do	0.05	3,000.
4	0.3	do	0.075	1,350.
5	0.3	Adipic-DETA-epi [2]	0.1	1,320.
6	0.3	do	0.3	5,400.
7	0.3	do	1.0	5,000.
8	0.3	DADM-AM Copolymer [3]	0.5	900.
9	0.3	do	0.75	1,020.
10	0.3	do	1.0	1,020.
11	0.3	Cationic starch [4]	0.8	1,140.
12	0.3	do	1.1	1,800.
13	0.3	do	1.4	3,040.
14	0.3	do	3.0	1,050.
15	0.3	Polyacrylamidoxime resin [5] with alum [6]	0.6	2,000.

[1] Based on dry weight of fibers.
[2] Adipic-DETA-epi=Adipic acid-diethylenetriamine epichlorohydrin prepared by Keim, U.S. Patent No. 2,926,154 (1960).
[3] DADM-AM copolymer=Copolymer of diallyl dimethyl ammonium chloride:acrylamide (11:89 weight ratio).
[4] Prepared by process of U.S. Patent No. 2,935,436 (1960).
[5] An amphoteric polymer prepared by method of U.S. Patent No. 2,959,574 (1960).
[6] 0.5% of alum based on the dry weight of the fibers added subsequent to the cationic resin.
[7] Drum temperature.

EXAMPLE 3

The following illustrates the manufacture of sized paper by use of the cationic polymer formed by reacting ammonium caseinate with alum.

The procedure of Example 2 is repeated except that ammonium caseinate (formed by reacting water-swollen casein with aqueous ammonia) and alum (added consecutively to the fibrous suspension) are employed in place of the cationic polymer of Example 2, and the fibers are sheeted at a basis weight of 200 lb./25" x 40"/500 ream. Electrophoretic tests show that the alum reacts with the ammonium caseinate as soon as it is added to the fibrous suspension, forming a cationic compound or complex.

Results are as follows.

Run No.	Percent Anionic Emul. Added [1]	Percent Ammonium Caseinate Added [1]	Percent Alum Added [1]	pH Adjustment [2]	Paper Lactic Acid Resist., Sec.
Control A	0.3	[3]	[3]	4.8	Inst.
Control B	0.3	[3]	0.9	4.8	Inst.
Control C	0.3	1.0	[3]	4.8	Inst.
1	0.3	1.0	0.9	4.3	3,300.
2	0.3	1.0	9.9	4.8	1,200.
3	0.3	1.0	0.9	6.0	1,310.

[1] On dry weight of fibers.
[2] After addition of alum.
[3] None.

EXAMPLE 4

The following illustrates the manufacture of sized paper according to the present invention by use of a normally anionic polymer rendered cationic by reaction with alum. The procedure of Example 3 is followed, and the paper is made at 200 lb. basis weight.

The polymer used is a 90:10 by weight acrylamide: acrylic acid copolymer which is rendered cationic by subsequent addition of alum.

Results are as follows.

Run No.	Percent Anionic Emul. Added [1]	Percent Polymer Added [1]	Percent Alum Added [1]	pH Adjustment [2]	Lactic Acid Resistance, Sec.
Control A	0.3	[3]	[3]	4.8	Inst.
Control B	0.3	1.0	[3]	4.9	Inst.
Control C	0.3	[3]	1.5	4.6	Inst.
1	0.3	1.0	1.5	4.7	185.
2	0.3	1.0	1.5	5.2	220.
3	0.3	1.0	1.5	6.0	340.
4	0.3	1.0	1.5	6.5	305.
5	0.3	1.0	1.5	7.0	300.

[1] On dry weight of fibers.
[2] After addition of the alum.
[3] None.

EXAMPLE 5

The following illustrates a full-scale mill run employing the process of the present invention.

An anionic sizing dispersion is prepared by rapidly stirring into 200 lb. of water at 85° C. 460 lbs. of a 5.4% by weight aqueous solution of gum ghatti 4.0 lbs. of powdered sodium lignosulfonate and 156 lbs. of molten distearic anhydride. The resulting crude emulsion (containing 5.8% distearic anhydride by weight) is passed through a continuous homogenizer and the product is discharged through a cooler into sufficient water at 20° C. to form a dispersion containing 1% by weight of distearic anhydride.

The resulting dispersion is fed into the intake line of the fan pump of a Fourdrinier machine making white bond paper at a basis weight of 50 lb. per 25" x 40"/500 ream. The furnish to the machine is 40% bleached softwood kraft, 35% bleached hardwood kraft, 20% bleached

sulfite, and 5% reprocessed broke, and contains 6% based on the dry weight of the fibers of filler clay and titanium dioxide and ½% alum on the same basis. The pH of the pulp is 6.2. The size dispersion is added in amount sufficient to provide 5 lb. of distearic anhydride per ton of fibers (dry basis).

Immediately upstream from the machine head-box is fed sufficient of a 1% by weight aqueous solution at pH 6.2 of the cationic water-soluble nonthermosetting polyamidepolyamine formed by condensing 1 mol of adipic acid with 1 mol of tetraethylenepentamine to form a polyamide, and reacting the polyamide in aqueous solution with 0.1 mol of epichlorohydrin, to provide 3 lb. of the polymer per ton of the fibers (dry basis).

The machine speed (rate of paper travel) is 800 ft./min. The dwell time of the paper in the drying section of the machine is about 3 minutes and the temperature of the steam to the drying drums varies from 200° F. to 250° F. In the machine, the web when nearly dry passes through a size press supplied with a 2% by weight aqueous solution of starch and is then lightly calendered. The paper is then substantially dry and is formed into a roll at about 150° F.

On leaving the papermaking machine, the paper has a sizing value of 950 seconds by the Tappi ink float method. This value is 1120 after the rolled paper has been stored 1 week, so that about 85% of the ultimate sizing of the distearic anhydride is developed on the machine.

EXAMPLE 6

The catalytic effect of the polyamidepolyamine resin upon paper-sizing fatty anhydrides is illustrated by the following.

A handsheet having an adsorbed content of a normally water-soluble cellulose-substantive cationic compound is prepared by adding 0.2% (solids based on the dry weight of the fibers) of a 10% by weight solution of the cationic 3 lb./ton polyamidepolyamine resin of Example 1 to an aqueous suspension of a 50:50 mixture of bleached softwood-bleached hardwood fibers at 0.5% consistency, sheeting the suspension in a handsheet machine to form a handsheet having a basis weight of 120 lb. per 25" x 15"/500 ream, and air dried until only faintly moist.

A control sheet is prepared in the same manner but without use of the resin.

Discs of equal size are cut from each of the handsheets and the discs are impregnated with a dispersion containing 0.2% distearic anhydride by weight, prepared in the same manner as the dispersion of Example 5. The discs are blotted so that each disc contains the same weight of distearic anhydride as the other. The discs are placed for 2 minutes in an oven at 230° F. and their sizing determined by use of 20% lactic acid applied at 100° F. by penescope under a 12" head to determine the on-the-machine sizing of the paper, and then the discs are placed in an oven at 105° C. for 60 minutes to determine the ultimate sizing of the discs. Results are as follows.

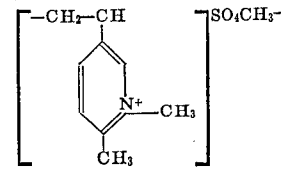
	Paper	
	Sizing, Seconds	
	No Cationic Resin	0.2% Cationic Resin
Minutes Heated:		
2	55	>7,200
60	>7,200	>7,200

These results obtained after the two minutes of heating show that the polyamide-polyamine resin produces a strong catalytic action.

EXAMPLE 7

The following further illustrates the catalyst-like action of cationic polymers in accelerating the rate at which the higher fatty acid anhydrides develop their sizing properties.

An aqueous suspension of well-beaten 70:30 bleached hardwood:bleached softwood kraft pulp at 0.6% consistency and pH 6 is divided into aliquots. To three of the aliquots are added sufficient of an aqueous solution of poly(1,2-dimethyl-5-vinyl)pyridinium methyl sulfate, composed of



linkages to provide 0.05%, 0.1% and 0.2% of the polymer based on the weight of the fibers. The aliquots were gently stirred to permit adsorption of the polymer by the fibers to go to substantial completion.

The pulps are formed into handsheets at a basis weight of 100 lb. per 25" x 40"/500 ream, together with an aliquot of the pulp which contained no polymer.

The handsheets are dried for two minutes on a laboratory drum drier having a surface temperature of 230° F. and are then impregnated with a 0.2% by volume solution of stearic anhydride in carbon tetrachloride. The resulting sheets which contain 0.2% by weight of stearic anhydride are mounted on a rack and the rack is placed for two minutes in a forced-draft laboratory oven having a temperature of 220° F.

The sizing properties of the resulting sheets are determined by placing 10 drops of 20% lactic acid solution (tinted with methylene blue) on each sheet and noting the percentage of the liquid which is absorbed in 30 minutes. Results are as follows.

Handsheets			Percent Lactic Acid Solution Absorbed After 30 Minutes [2]
No.	Percent Cationic Polymer [1]	Percent Stearic Anhydride [1]	
1	(3)	(3)	100
2	0.05	(3)	100
3	0.1	(3)	100
4	0.2	(3)	100
5	(3)	0.2	70
6	0.05	0.2	0
7	0.1	0.2	10
8	0.2	0.2	15

[1] Based on dry weight of fibers.
[2] Estimated.
[3] None.

We claim:

1. A process for the manufacture of sized paper which comprises separately adding an aqueous anionic dispersion of hydrophobic organic cellulose-reactive paper sizing carboxylic anhydride particles to an aqueous suspension of cellulose papermaking fibers and a water-soluble cellulose-substantive cationic polyamine having a molecular weight in excess of 1,000, the amount of said polyamine being at least sufficient to deposit said anhydride particles on said fibers and to accelerate the rate at which said anhydride develops its sizing properties on cellulose fibers at 190° F.-250° F., sheeting said suspension to form a water-laid web, and drying said web at a temperature between 190° F. and 250° F.

2. A method according to claim 1 wherein the cationic cellulose-substantive compound is added subsequent to the addition of said anionic dispersion.

3. A process according to claim 1 wherein the pH of the fibrous suspension during addition of said cationic compound is between 5 and 8.

4. A process according to claim 1 wherein a small amount of alum, up to 5% of the dry weight of the fibers, is added as extender for said polyamine.

5. A process according to claim 4 wherein the alum is added subsequent to addition of the anionic dispersion and the water-soluble cellulose-substantive cationic polyamine.

6. A process according to claim 1 wherein the water-soluble cellulose-substantive cationic compound is a water-soluble linear polymer having a substantial proportion of —CH_2CH_2—NH— linkages.

7. A process according to claim 1 wherein the water-soluble cellulose-substantive cationic compound is a tetraethylenepentamine-epichlorohydrin resin.

8. A process according to claim 1 wherein the water-soluble cellulose-substantive cationic compound is an adipic acid - polyalkylenepolyamine - epichlorohydrin polymer.

9. A process according to claim 1 wherein the water-soluble cellulose-substantive cationic compound contains at least one amino group for every 10 carbon atoms in said compound.

10. A process according to claim 1 wherein the paper-sizing carboxylic anhydride is distearic anhydride.

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