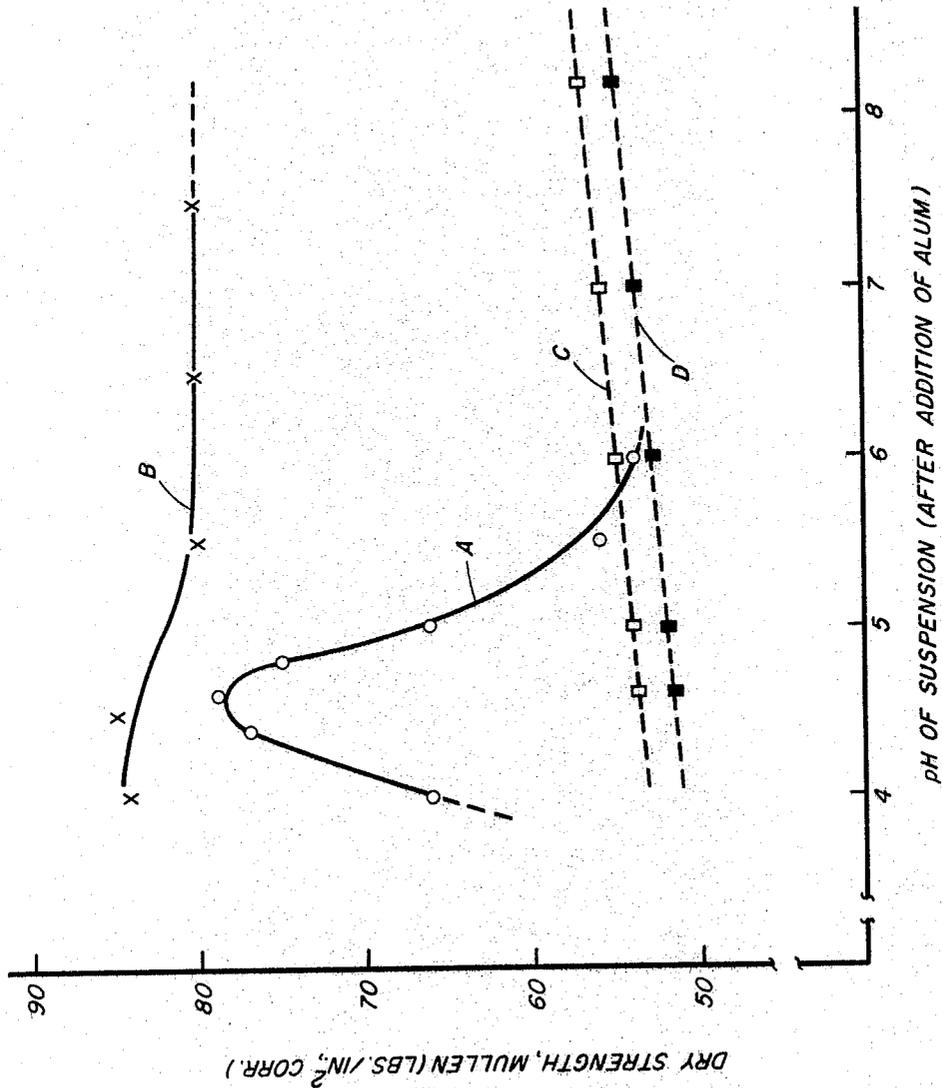


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PROCESS OF FORMING DRY STRENGTH PAPER WITH
CATIONIC RESIN, POLYACRLAMIDE RESIN AND
ALUM COMPLEX AND PAPER THEREOF
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3,332,834



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3,332,834

PROCESS OF FORMING DRY STRENGTH PAPER WITH CATIONIC RESIN, POLYACRYLAMIDE RESIN AND ALUM COMPLEX AND PAPER THEREOF

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10 Claims. (Cl. 162-164)

This is a continuation-in-part of my copending application Serial No. 368,444 filed on May 7, 1964 and now abandoned.

The present invention relates to an improved method for manufacturing paper of high dry tensile strength but of low wet tensile strength, by use of an anionic polyacrylamide dry strength resin. The invention includes the process involved, and the resulting paper.

Azorlosa Canadian Patent No. 477,265 of September 25, 1951, discloses that paper of improved dry strength but of low wet tensile strength is produced when an anionic polyacrylamide (preferably a 90:10 acrylamide: acrylic acid copolymer) is deposited on cellulose fibers at pH 4.5 in aqueous suspension by the action of a water-soluble polyvalent metal salt (for example, alum). In the process, the pH of 4.5 is critical, because the strengthening action of the polyacrylamide is largely lost when the suspension is sheeted at a pH only a few points different therefrom.

The discovery has now been made that paper of high dry strength and of low wet strength is obtained when the anionic polyacrylamide is applied to the fibers in conjunction with (a) a water-soluble non-thermosetting resin having a molecular weight less than 30,000 and (b) alum. Alum (or other equivalent polyvalent metal salt) is essential for the aforementioned results.

The process of the present invention in preferred embodiments possesses the following advantages:

(1) It greatly increases the dry strength imparted by the dry strength resin.

(2) it decreases by about two-thirds the amount of alum needed to set the resin on the fibers.

(3) It permits the dry strength resin to be deposited on the fibers in the neutral pH range (e.g., 5-8). The process thus does not necessarily produce paper which undergoes acid tendering on aging.

More in detail, according to the invention there is first formed an aqueous suspension of cellulose papermaking fibers. There is then added to the suspension an aqueous solution of an anionic polyacrylamide dry strength resin, alum or an equivalent salt, and a cationic non-thermosetting resin. Preferably the suspension has a consistency of 1/2%-5% during addition of the agents.

The agents may be added in any sequence with substantially the same results. If desired, the cationic resin can be added in admixture with the alum. The agents may be added at any point prior to sheet formation, but best strength is generally obtained when one of the resins is added at the fan pump or head box.

Sized paper can be manufactured by adding rosin size to the fibrous suspension. The rosin size should be added at such point in the papermaking system that it is set on the fibers prior to addition of the cationic resin. Thus rosin size and the anionic resin may be added to the

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refined stock chest, the alum at the fan pump, and the cationic resin at the head box.

The pH of the fibrous suspension may be in the neutral or alkaline range (pH 5-8) during addition of some or all of the agents. This permits a closed neutral paper-making cycle which produces paper having a neutral or nearly neutral pH. Best dry strength (based on the combined weight of the two resins) is generally obtained when the resins are added within roughly the weight ratio range of 20:80 and 80:20. The amount of alum added is typically 1/3 to 1/6 of the minimum amount heretofore found necessary to set anionic polyacrylamide dry strength resins on cellulose fibers. Thus in the past it has been necessary to use at least 1.5% of alum based on the weight of the fibers, but in accordance with the present invention no more than 1/3 of this amount (0.3%) is needed.

In the absence of added sizing agent, the total amounts of the anionic dry strength resin and the cationic fixing agent depend upon the amount of dry strength which it is desired to impart to the paper. About 1/2% each of these resins, based on the dry weight of the fibers, causes a substantial improvement, and evidently still smaller amounts are useful. Larger amounts of the two resins up to a total of 3%-5% on the dry weight of the fibers may be added with development of increasing dry strength, so that evidently larger amounts provide additional benefit.

The optimum ratio of the cationic resin to the anionic polyacrylamide resin, and the optimum proportion of alum to these resins vary from instance to instance depending for example, on the molecular weight and anionic properties of the resins, the acidity of the pulp, and the pH of the aqueous phase, and are most easily determined by laboratory experimentation as shown in the examples which follow. However, the alum and the cationic resin are each added in amount between 1/10% and 5% of the dry weight of the fibers, and together are added in sufficient amount to deposit the anionic polymer (and any anionic size present) on the fibers; the cationic resin, the anionic polyacrylamide resin, and the alum are deposited as a complex on the fibers.

In the process of the present invention, the anionic polyacrylamide dry strength resin acts as primary dry-strength resin and the cationic resin and alum act as fixing agents for the dry strength resin, i.e., as agents which "fix" or deposit the resin on the fibers. Since neither the alum nor the cationic resin contributes significant dry strength, the present invention is evidently the result of the discovery of a pronounced synergistic action. Neither the mechanism of this reaction nor the manner in which the agents are related in the finished sheet are known, and applicant does not wish to be bound by any theory.

The fibrous paper-making suspension may be sheeted at any acid pH above about 4, but in most instances a pH of 6 gives best dry strength and is therefore preferred. The process is not pH sensitive, and any pH in range of 5.5-6.5 is very satisfactory.

The process may be employed in conjunction with other materials customarily used in the manufacture of paper. Thus anionic agents (for example, rosin size, fertilized rosin size, anionic dyes, and anionic wax sizes) can be added along with the polyacrylamide dry strength resin. The amount of alum added should be increased as needed to set these materials on the fibers.

If desired, other cationic materials may be added along with the alum, the cationic fixing agent, or both. Thus, there may be added nonionic emulsions of heretofore known nonionic sizing agents, for example, wax size, octadecyl ketene dimer, stearic anhydride, etc. In addition, there may be added cationic sizes, for example, the size prepared by reacting triethylenetetramine with stearic acid followed by solubilization by addition of acetic acid as shown in U.S. Patent No. 2,772,969, the higher aliphatic amine-epichlorohydrin sizes of U.S. Patent Nos. 2,694,629 and 2,694,630, and cationic emulsions of the aforementioned non-ionic sizes. In the latter event it is advantageous to employ a nonthermosetting cationic resin as the emulsifying agent, as is shown in one of the appended examples.

When the cationic emulsion contains enough of a cationic resin to deposit the anionic component or components on the fibers, separate addition of a cationic resin is not necessary.

A number of anionic polyacrylamide dry strength resins are known. Some are disclosed in said Azorlosa patent. In general, they are vinyl polymers at least 80 mol percent composed of $-\text{CH}_2\text{CH}(\text{CONH}_2)-$ linkages. They include the water-soluble or water-dispersible polymers and copolymers of acrylamide with acrylic acid or methacrylic acid, for example itaconic acid, maleic acid, fumaric acid, citraconic acid, acrylamide-acrylic acid, acrylamide-acrylonitrile-acrylic acid; copolymers of acrylamide with one of the lower alkyl or vinyloxyalkyl acrylates and acrylic acid, or with the lower alkyl vinyl ethers and acrylic acid; and similar copolymers in which methacrylic acid or itaconic acid is substituted in place of acrylic acid in the above examples. They include copolymers of styrenesulfonic acid with acrylamide.

Exemplary of the acrylic type polymers and copolymers which may be utilized herein are those described in U.S. Patent 2,661,309 to Julian L. Azorlosa and Canadian application Ser. No. 297,013, Julian L. Azorlosa, filed Feb. 1, 1950, now Patent No. 247,577.

The water-soluble or water-dispersible compounds which may be utilized herein also include condensates of the foregoing polymers with lower alkylene oxides for example ethylene oxide and propylene oxide. In the aforementioned polymers the amide and carboxy substituents are the primary functional substituents and the remaining substituents act as spacers or as solubilizing substituents.

Preparation of these carboxyl-containing polymers and copolymers and the condensation of same with alkylene oxides may be carried out by well-known procedures. In the latter reaction, the proportion of alkylene oxide introduced may vary from 1 mol percent to 250 mol percent, and preferably from about 10 mol percent to about 95 mol percent of the carboxyl-containing units of the polymer.

A variety of water-soluble non-thermosetting cationic resins are known which have suitable molecular weights and which in general are suitable for use in the process of the present invention, for example, low molecular weight polyethylenimine and polyvinylamine. There can also be used the adipic acid-tetraethylenepentamine-epichlorohydrin resin of Strazdins application Serial No. 281,321, filed May 17, 1963; the methylamine-ethylene-diamine(or-ammonia)-epichlorohydrin resin, adipic acid-tetraethylenepentamine-epichlorohydrin resin, and other resins of Woodberry et al., application Serial No. 341,413, filed on January 30, 1964 now Patent No. 3,258,393; the resin prepared by condensing ethylenedichloride with 3,3'-iminobispropylamine, the quaternized polyacrylamide resins of U.S. Patent No. 2,884,057; the Hoffman degradation products of polyacrylamide prepared as shown in U.S. Patent No. 2,890,978, and the acrylamide-vinylpyridine copolymer of U.S. Patent No. 2,963,396.

The condensation products of polyfunctional amine with cross-linking agents such as epichlorohydrin and

ethylene dichloride in general are prepared by adding the linking agent to the polyfunctional amine in increments, each increment being substantially completely reacted before the next increment is added, and terminating the addition of cross-linking agent when the reaction mixture is close to gelation. Addition of the cross-linking agent is preferably stopped before the resin achieves a molecular weight of about 10,000; when this is done the resin is virtually without capacity to impart wet strength under ordinary paper-making conditions. The last increment of cross-linking agent is allowed to react substantially to completion. The resulting resin is consequently substantially non-thermosetting. If desired, resins may be used which have a molecular weight as high as about 30,000. Paper containing ordinary amounts of resins of this molecular weight possess commercially insignificant wet strength. Such paper has a wet strength which is less than 10% of its dry strength, and consequently can be pulped by the use of ordinary mechanical pulping devices without need for treatment with steam jets or special chemicals. Resins having molecular weights in much beyond about 30,000 are not suitable because they may impart significant wet strength to paper. The molecular weights of such resins can be determined by the light scattering method. A more convenient method is to test the resins to determine their wet strengthening properties. This may be done by adding 0.5% of the resin (dry fiber basis) to a pulp of paper-making fibers at pH 7, sheeting the pulp to form a wet web, drying the web at 100° C., and determining the strength of the web after soaking in water.

In place of alum there may be used aluminum chloride and aluminum nitrate.

The invention will be further illustrated by the examples which follow. These are preferred embodiments of the invention, and are not to be construed in limitation thereof.

Example 1

The following illustrates the comparative effect of the added cationic resin in broadening the pH range over which the anionic resin exerts its strengthening effect.

For this work a neutral 50:50 bleached soft wood-bleached hard wood pulp is employed beaten to a Canadian standard freeness of 510 ml. Two portions are removed.

Series A.—To one of the portions is added 2% of alum based on the dry weight of the fibers. Seven aliquots are taken and the pH of each is adjusted to the values shown in the table below. To each of the aliquots 0.35% of a 90:10 polyacrylamide:polyacrylic acid dry strength copolymer resin is added based on the dry weight of the fibers. The molecular weight of the copolymer is about 200,000. The fibers in the aliquots are formed into handsheets on a Nash handsheet machine at a basis weight of about 100 lb. per 25" x 40"/500 ream, and the handsheets are dried by two passes of 1.5 minutes each on a laboratory drum drier having a drum temperature of 240° F. The results are tabulated below and are shown in the attached drawing as Curve A.

Series B.—The foregoing procedure is repeated except that 0.15% of a low molecular weight nonthermosetting cationic adipic acid-tetraethylenepentamine-epichlorohydrin resin is mixed into the pulp before addition of the anionic resin.

The cationic resin is prepared by reacting 1 mol of adipic acid with 1 mol tetraethylenepentamine without solvent at 153° C. substantially completely (to a viscosity of 1300 cp.), diluting to 35% solids with water, adding 0.3 mol of epichlorohydrin and maintaining the mixture at 80° C. until reaction of the epichlorohydrin is substantially complete. The product has a viscosity of 100 cp. at 80° C. and is adjusted to pH 6.

The results are tabulated below and are shown in the attached drawing as Curve B.

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SERIES A

Run No.	Percent Alum ¹	pH Adj.	Anionic D/S Resin ¹	Percent Cationic Fixing Agent	Dry Burst Strength, ² lb./in. ³
1-----	2.0	4.0	0.35	None	66
2-----	2.0	4.4	0.35	do	77
3-----	2.0	4.6	0.35	do	79
4-----	2.0	4.8	0.35	do	75
5-----	2.0	5.0	0.35	do	68
6-----	2.0	5.5	0.35	do	56
7-----	2.0	6.0	0.35	do	54

SERIES B

Run No.	Percent Alum ¹	pH Adj.	Anionic D/S Resin ¹	Percent Cationic Fixing Agent	Dry Burst Strength, ² lb./in. ³
8-----	1.0	4.0	0.35	0.15	84
9-----	1.0	4.5	0.35	0.15	85
10-----	1.0	5.5	0.35	0.15	80
11-----	1.0	6.5	0.35	0.15	80
12-----	1.0	7.5	0.35	0.15	80

¹ Based on dry weight of the fibers.
² Corrected to 100 lb. basis weight. In each instance the wet strength of the sheets is less than 10% of their dry strength.
³ Value to which pH of suspension is adjusted after addition of alum.

Curve A shows that while the anionic polyacrylamide resin produces an excellent improvement in dry strength when fixed on the fibers by the action of alum, the improvement takes place only when the paper is made (i.e., when the fiber bonds are formed) at about pH 4.5. The curve shows that the strength imparted by the resin is comparatively poor when the paper is made at pH 4.0 and at pH 5.0.

Curve B shows that paper of even better dry strength is produced by the action of the same amount of dry strength resin over the pH range which extends from below 4.0 to above 7, provided that a small amount of a cationic non-thermosetting resin is present. The cationic resin thus removes a critical restriction from the paper-making operation without sacrifice of results.

Curve C represents typical strength values of paper made by use of 2% alum and 0.15% of the cationic resin, and Curve D shows typical strength values of raw paper (i.e., paper which contains no additives at all other than alum).

Comparison of Curve C with Curve D shows that the strengthening imparted by the alum and the cationic resin (the distance between the two curves) is negligible compared with the improvement which is effected by these materials in combination with the anionic copolymer. The comparison thus shows that the cationic resin produces a synergistic action.

Example 2

The following illustrates in greater detail the effect of the added water-soluble resin in increasing the pH over which anionic polyacrylamide dry strength resin exert their strengthening effect when fixed on the fibers in the presence of dissolved alum.

A 50:50 bleached hardwood: bleached softwood pulp is beaten to a Canadian standard freeness of 500 ml. and diluted to 0.6% consistency. Seven aliquots are removed and are treated as shown in the table below. In each instance the materials added are added separately as dilute (1%-5%) aqueous solutions with gentle stirring, in the sequence shown in the table, reading from left to right. In each instance the pH of the pulp, after addition of the alum, is adjusted to the value shown in the table.

The aliquots are then formed into handsheets having a basis weight of 50 lb. The handsheets are dried for one minute on a laboratory drum drier having a drum temperature of 240° F. and their dry strength is determined by means of the Mullen tester.

Results are as follows: Runs 1-5 are controls, and Runs 6-11 illustrate the present invention. In each instance the wet strength of the test sheets is less than 10% of their dry strength.

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Run No.	Anionic D/S Resin Added, Percent ¹	Alum Added, Percent ¹	Pulp pH ²	Cationic Resin Added, Percent ¹	Dry Strength (Mullen, lb./in. ²)
5					
1-----	None	1.5	4.5	None	25
2-----	0.5	1.5	4.5	do	39
3-----	None	1.5	4.5	0.3	26
4-----	0.5	1.5	4.5	None	27
5-----	0.5	1.5	6.0	do	26
10					
6-----	0.5	0.5	4.5	0.3	44
7-----	0.5	0.5	5.0	0.3	43
8-----	0.5	0.5	6.0	0.3	43
9-----	0.5	0.5	7.0	0.3	43
10-----	0.5	0.5	8.0	0.3	42
11-----	0.3	0.5	6.0	0.3	40

¹ Based on dry weight of fibers.
² Adjusted after addition of alum and before addition of cationic resin (when added). The pH does not change significantly thereafter.

Example 3

The following illustrates the effect the cationic resin has in decreasing the amount of alum needed to set the anionic resin on the fibers.

The general procedure of Example 1 is repeated except that the pulp used is composed of 100% bleached southern pine fibers beaten to a Canadian standard freeness of 630 ml. Results are as follows. Runs 1 and 2 are control runs, and Runs 3-6 illustrate the process of the present invention.

Run No.	Anionic D/S Resin Added, Percent ¹	Alum Added, Percent ¹	Pulp pH ²	Cationic Resin Added, Percent ¹	Dry Strength (Mullen, lb./in. ²)
30					
1-----	0.3	0.5	6.0	None	45.5
2-----	0.3	None	6.0	0.2	46.5
35					
3-----	0.3	0.5	6.0	0.2	60.0
4-----	0.3	0.4	6.0	0.2	59.5
5-----	0.3	0.3	6.0	0.2	58.5
6-----	0.3	0.15	6.0	0.2	58.0

For footnotes 1 and 2 see table of Example 2 above.

Comparison of the results of Runs 2-6 with the results of Run 1 show that the presence of the cationic resin permits the amount of alum to be decreased by 70% while producing paper of higher dry strength. In Run 5, the amount of alum would be insufficient to fix the anionic dry strength resin on the fibers in the absence of the cationic resin.

Example 4

The following illustrates the comparative effect of different nonthermosetting cationic resins as agents increasing the pH range over which the polyacrylamide-alum combination produces its strengthening action.

The procedure of Run 8 of Example 2 is repeated, except that in each instance a different nonthermosetting cationic resin is employed, as shown by the table below.

Run No.	Cationic Resin Added—Components ¹	Molar Ratio	Dry Strength Mullen, lb./in.
60			
1-----	Adipic acid-DETA-epichlorohydrin...	1:1:0.4	43.3
2-----	Adipic acid-TEPA	1:1	40.0
3-----	DETA-ethylene dichloride	1:1	37.0
4-----	Ethylene diamine-epichlorohydrin	1:1	39.5
65			
5-----	Methylamine-NH ₂ -epichlorohydrin	1:1	45.4
6-----	NH ₃ -epichlorohydrin	1:1	49.5
7-----	Polyethylenimine, low M.W. (half quantity used).	-----	36.5

¹ DETA-diethylenediamine; TEPA-tetraethylenepentamine. The components are reacted to substantial completion.

In each instance the wet strength of the test sheets is less than 10% of their dry strength.

Example 5

The following illustrates the manufacture of rosin-sized paper according to the present invention.

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The procedure of Run 6 of Example 2 is repeated, except that 1% of rosin size is added simultaneously with the dry strength resin, and the amount of alum is increased to 1.25% of the dry weight of the fibers. Well-sized paper of high dry strength is obtained. The paper has substantially no wet strength.

Example 6

The following illustrates the preparation of sized, high dry-strength paper according to the present invention by use of cellulose-reactive sizing agents in aqueous anionic emulsion state.

The procedure of Run 6 of Example 2 is repeated except that there is added along with the dry strength resin sufficient of a 10% aqueous anionic emulsion of stearic anhydride (prepared by emulsifying at 90° C. stearic anhydride in water containing sodium lignosulfonic acid is emulsifying agent and then homogenizing) to provide 0.3% of the stearic anhydride based on the dry weight of the fibers. A well-sized sheet of high dry strength is obtained which possesses virtually no wet strength.

The foregoing procedure is repeated except that the size is a 10% aqueous solution of octadecyl ketene dimer prepared by the emulsification procedure described above. Similar results are obtained.

Example 7

The following illustrates the preparation of sized, high dry-strength paper according to the present invention by use of a cationic emulsion of a cellulose-reactive sizing agent, the cationic agent in the emulsion being a low molecular weight nonthermosetting cationic dry strength resin required by the present invention.

An aqueous suspension is prepared at 0.6% consistency from a 50:50 mixture of bleached:unbleached northern kraft fibers. To this is added ½% of alum based on the dry weight of the fibers, and the pH of the suspension is adjusted to 6. There is then added an aqueous cationic emulsion of stearic anhydride formed by emulsifying 10 g. of stearic anhydride in about 50 g. of water at 90° C. water containing 15% by weight of the nonthermosetting adipic acid-triethylenepentamine-epichlorohydrin resin described above, homogenizing the emulsion hot, chilling and diluting with water to 10% solids. The amount of the emulsion which is added is sufficient to provide 0.25% of stearic anhydride and 0.375% of the cationic agent based on the dry weight of the fibers.

The suspension is sheeted to form a wet web having a basis weight of 101.2 pounds per 25" x 40"/500 ream, and the web is dried at 100° C. for 3 minutes. The resistance of the resulting paper to penetration by hot 20% aqueous lactic acid at a 12" head is determined by penetrometer, and the dry strength of the sheet is determined by the Mullen tester. The lactic acid resistance of the sheet is 1135 seconds; its bursting strength (Mullen) (adjusted to 100 pounds basis weight) is 55.5 lb./in.².

The foregoing procedure is repeated except that 0.25% based on the dry weight of the fibers of a 90:10 acrylamide:acrylic acid dry strength copolymer is added after addition of the alum, and before addition of the stearic anhydride emulsion.

The lactic acid sizing increases to 2245 seconds and Mullen bursting strength to 73.5 lb./in.².

The results show that the anionic polyacrylamide resin acts as fortifying agent for the stearic anhydride.

Example 8

The procedure of Example 7 is repeated except that octadecyl ketene dimer is employed in place of the stearic anhydride. A similar improvement is obtained.

Example 9

The procedure of Example 7 is repeated, except that the stearic anhydride is replaced by octadecyl isocyanate

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and the emulsification temperature is 40° C. A similar improvement is obtained.

Example 10

The procedure of series B of Example 1 is repeated, except that 1 mol of triethylenetetramine is used in place of the 1 mol of tetraethylenepentamine disclosed therein. Results are substantially the same.

Example 11

The following illustrates the improvement issued by the present invention in the mill scale manufacture of wood board.

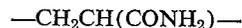
At the start of the trial, the mill is operating on a furnish of bleached Southern hard wood and pine kraft process fibers in 50:50 ratio, and to the furnish at the machine chest is being added 1.28% of rosin size and 1.33% of alum based on the dry weight of the fibers.

The amounts of rosin size and of alum which are added are each decreased to 1% (decreases of 22% and 25% respectively), and there is added to the regulator box 0.3% solution of a 90:10 acrylamide:acrylic acid copolymer in amount sufficient to supply 0.3% of the copolymer on the dry strength of the fibers. There is added to the fan pump 0.2% based on the dry weight of the fibers of a water-soluble condensation product of 1 mol of adipic acid and 1 mol of tetraethylenepentamine substantially completely reacted with 0.3 mol of epichlorohydrin.

As a result of the foregoing changes, the pH of the fibrous suspension increases from 4.5 to 5, the Mullen test of the board produced by the mill increases by 15%, the internal board strength increases by 36%, and the lactic acid resistance of the board (as determined by the Cobb test) increases by 25%.

I claim:

1. A process for the manufacture of high dry-strength paper having substantially no wet strength, which comprises adding a water-soluble anionic dry strength vinyl polymer at least 80 mol percent composed of



linkages, alum and a water-soluble substantially nonthermosetting cationic resin having a molecular weight between about 1000 and about 30,000, to an aqueous suspension of cellulose paper-making fibers thereby forming a complex of said anionic polymer, alum, and cationic resin on said fibers, sheeting said fibers at a pH between 4 and 8 to form a web, and drying said web; the amount of said alum and said cationic resin each being between ½% and 5% of the dry weight of the fibers and being together sufficient to deposit said anionic polymer on said fibers.

2. A process according to claim 1 wherein said anionic resin is substantially composed of $-\text{CH}_2\text{CH}(\text{CONH}_2)-$ and $-\text{CH}_2\text{CH}(\text{COOH})-$ linkages in molar ratio between 95:5 and 85:15.

3. A process according to claim 1 wherein the cationic resin is a substantially completely reacted 1:1:0.4 molar ratio adipic acid:tetraethylenepentamine:epichlorohydrin resin.

4. A process according to claim 1 wherein the cationic resin is a substantially completely reacted 1:0.2:1.3 molar ratio methylamine:ammonia:epichlorohydrin resin.

5. A process according to claim 1 wherein the cationic resin has a molecular weight less than 10,000.

6. A process according to claim 1 wherein said vinyl polymer is deposited on said fibers at a pH between 5 and 7.

7. A process according to claim 1 wherein an anionic size is added to said suspension along with said vinyl polymer, and the size is set on the fibers by the action of alum.

8. A process for the manufacture of sized high dry strength paper having substantially no wet strength, which

comprises adding to an aqueous suspension of cellulose paper-making fibers a water-soluble anionic dry strength vinyl polymer at least 80 mol percent composed of $-\text{CH}_2\text{CH}(\text{CONH}_2)-$ linkages, alum, and an aqueous cationic dispersion consisting essentially of a hydrophobic cellulose-reactive paper size as dispersed phase in an aqueous phase having a dissolved content of a nonthermosetting cationic dry strength resin having a molecular weight between about 1000 and about 30,000 as agent rendering said dispersion cationic thereby forming a complex of said polymer, alum, and resin on said fibers, sheeting said fibers at a pH between 4 and 8 to form a web, and drying said web at a temperature above about 190° F.; the amount of said alum and said cationic resin each being between $\frac{1}{10}\%$ and 5% of the dry weight of the fibers and being together sufficient to deposit said anionic polymer on said fibers.

9. A process according to claim 8 wherein said alum is added before, and said aqueous cationic dispersion is added after addition of said dry strength vinyl polymer, the molecular weight of said cationic dry strength agent being less than about 10,000.

10. Paper of improved dry strength but of substantially no wet strength, composed of water-laid cellulose fibers bonded together by a uniformly adsorbed content of a complex consisting essentially of a normally water-soluble anionic dry strength vinyl polymer at least 80 mol percent composed of $-\text{CH}_2\text{CH}(\text{CONH}_2)-$ linkages, alum, and a normally water-soluble non-thermosetting cationic resin having a molecular weight between about 1000 and about 30,000 said paper having a pH between 4 and 8; the amount of said alum and said cationic resin each being less than 5% of the dry weight of the fibers.

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S. LEON BASHORE, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,332,834

July 25, 1967

Walter Florus Reynolds, Jr.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 61 and 62, for "fertified" read -- fortified --; column 4, line 67, for "mol" read -- mol of --; column 5, line 26, for "the", third occurrence, read -- this --; column 6, in the third table, fourth column, line 5 thereof, for "45.4" read -- 45.5 --; column 8, line 19, for "dosin" read -- rosin --.

Signed and sealed this 18th day of June 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents