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DRY STRENGTH PAPER

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The present invention relates to paper of substantially improved dry strength resulting from a small adsorbed content of a linear carbon chain polymer containing carbamyl and hydroxyamidino side groups, as the fiber bonding agent. More particularly the present invention relates to such paper having low wet strength.

In recent years a demand has arisen in the paper industry for paper which has high dry strength but low wet strength, so that it can be repulped in papermill beater equipment without need for treatment with caustic pulping agents, steam jets, etc. Paper stock having this property is particularly desired for conversion into letter paper, check paper, book paper, newspaper and envelopes, which do not become wet during normal use.

The discovery has now been made that paper composed of a waterlaid web of cellulosic papermaking fibers bonded together by a small adsorbed amount of a normally water-soluble linear carbon chain polymer containing carbamyl and hydroxyamidino side groups (as more particularly hereinafter described) possesses substantially improved dry strength and yet possesses low wet strength. In preferred instances the dry tensile strength of paper of the present invention is improved by about 50%–75% as a result of the strengthening action of the polymer, and dry burst values are improved by upward of 75%–85%. On the other hand, the paper (at ordinary book paper weight) possesses a wet tensile strength of less than about 3 lbs./in., which means that it can be repulped in ordinary papermill equipment.

The polyacrylamidoxime polymer of the present invention is soluble in water yet is substantively adsorbed therefrom by cellulose fibers. Accordingly, paper of the present invention is manufactured by forming an aqueous suspension of papermaking cellulosic fibers, adding thereto a small amount of an aqueous solution of polyacrylamidoxime polymer, sheeting the fibers to form a cellulosic web, and heating the web until dry. The polymers of the present invention are non-thermosetting and thus do not require heat for development of their strengthening properties. However, they are thermostable and thus the wet webs may be dried without harm on steam-heated rolls in the customary temperature range of 190° F. to 250° F.

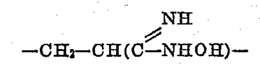
Only a small amount of polymer need be added. A substantial effect is noted with as little as 0.1% based on the dry weight of the fibers. The strengthening effect levels off when more than about 5% is added, and most efficient use of the polymer is in the range of about 0.5%–2% which is therefore preferred.

In the process, the polymer is well adsorbed by fibers which have been rosin sized, and the beneficial effect of the polymer in increasing the dry strength is not significantly diminished by the presence of such sizing on the fibers. It is an important advantage of the invention that the polymer acts synergistically with the rosin size, greatly increasing the water resistance imparted by the size.

The polyacrylamidoxime polymer of the present invention is ampholytic, and thus may be applied as an anionic or cationic material. It is insensitive to pH and affords substantially the same results at pH 6.5 as at pH 3.5. The evidence is that somewhat better dry strength is developed when the pH of the suspension during addition of the polymer is between 4.5 and 6.5, and this range accordingly is preferred.

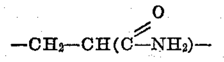
Best dry strength values are usually obtained when the fibrous suspension during addition of the polymer contains alum. Since the polymer is self-substantive the alum does not appear to act as mordant or precipitant. Evidently the paper produced from suspensions containing alum carries the polymer in the form of an alum complex. About ¼% of dissolved alum in the suspension (based on the dry weight of cellulose fibers) is sufficient to cause a substantial increase in the dry strength imparted by the resin, and more than about 2% appears to be unnecessary for the purpose. An intermediate amount in the range of ½%–1½% is accordingly preferred, it being understood that much larger amounts may be present without harm. With or without alum, adsorption of the polymer by the fibers is substantially complete.

The polymer employed in the present invention consists predominantly of hydroxyamidinoethylene and carbamylethylene linkages, the theoretical formulae of which are



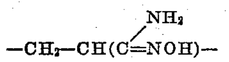
$$-CH_2-CH(\overset{NH}{\overset{\|}{C}}-NHOH)-$$

and



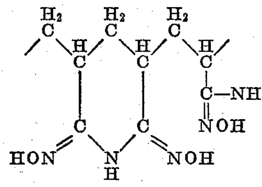
$$-CH_2-CH(\overset{O}{\overset{\|}{C}}-NH_2)-$$

The former linkage may exist in the tautomeric form



$$-CH_2-CH(\overset{NH_2}{\overset{|}{C}}=NOH)-$$

and moreover two adjacent hydroxyamidino substituents may react or coordinate to form a linkage of the type



Paper containing polymers having such linkages is within the scope of the invention.

It is within the scope of the invention to employ polymers containing additional groups which act as diluents, or spacers, or which act in known manner for other purposes. Then the polymer chain may carry in minor proportion alkyl or aryl, alkoxy, hydroxyl, carboxyl, ester, amine, carboxy, quaternary ammonium, and nitrile groups as supplemental substituents. Up to 50 mol percent of such substituents may be present, it being understood that in the case of the hydrophobic substituents the amounts thereof should be limited so that the polymer remains water-soluble to the extent of at least 5%.

The hydroxyamidino and carbamyl groups of the polymer are active ionically and evidently serve two principal functions. The first is to provide electrostatic loci, capable of acting ionically by which the polymer macromolecule as a whole is attracted to and substantively adsorbed by cellulose fibers in aqueous suspension in the presence or absence of dissolved polyvalent metal salts. The second function is to provide dry strength. The evidence is that the amide (—NH_2 or =NH) component coordinates with the surface of the fibers or the anhydroglucose units therein and is responsible to some extent at least for the dry strength imparted by the polymer.

The hydroxyamidino grouping is effective electrostatically in very small amounts and as little as 1% based on the remaining substituents present has been sufficient to render the macromolecule cationically active and self-substantive to cellulose. Considerable improvement in the dry strength is obtained by use of polymers containing a larger proportion of these groupings, particularly when the polymer contains hydroxyamidinoethylene and carbamylethylene linkages in ratio between about 1:10 and 3:10. Increasing the proportion of hydroxyamidino groups in the macromolecule results in further improvement in dry strength. This improvement, however, becomes progressively less as the proportion rises above this ratio range and accordingly the range stated is regarded as the practical maximum.

The carbamylethylene linkages which constitute the other major functional grouping in the polymer are ionically inert, but powerfully coordinate or react with the cellulose to provide dry strength. Apparently for the latter purpose they are somewhat more effective than the hydroxyamidinoethylene linkages, and accordingly, the number of carbamylethylene linkages should be at least 10% of the number of hydroxyamidinoethylene linkages. The polymers employed in the present invention may be prepared in any convenient manner. In practice they are most conveniently prepared by copolymerizing a water-soluble vinyl nitrile and a water-soluble vinyl amide in major proportion with or without supplementary or diluent vinyl material to form an essentially linear carbon chain amide-nitrile polymer. Part or all of the nitrile groups are then reacted with hydroxylamine to form hydroxyamidino groups in the proportion specified. It is preferred to form the polymer by copolymerizing acrylonitrile (methacrylonitrile, crotononitrile, etc.) with acrylamide or similar amide having an unsubstituted —NH_2 amide substituent in molar ratio between about 70:30 and 90:10 and then heating with hydroxylamine to convert nitrile groups to hydroxyamidino groups in proportion specified above. The polymer may be subjected to other reactions before or after the hydroxylamine reaction, and thus any ester groups present may be subjected to hydrolysis to form hydroxy or acid groups; any nitro groups present may be reduced to amine groups; any chloro groups may be reacted with tertiary amines to form quaternary ammonium groups.

The vinyl polymerization leading to formation of the linear chain polymer may be performed in aqueous medium using a redox catalyst, and molecular growth to an advanced stage should be favored. The development of increased dry strength requires the use of polymers having a molecular weight in excess of about 100,000 (as determined by the Staudinger method based on viscosity) and considerably better results are obtained when the molecular weight is upwards of 500,000, which is the preferred lower limit. Generally the polymers are too viscous for commercial use at molecular weights in excess of 5,000,000 and this therefore is the maximum of the preferred range.

The invention will be more particularly described by the examples which follow. These examples illustrate specific embodiments of the invention and are not intended as limitation thereon.

Example 1

The following illustrates the manufacture of paper of excellent dry tensile strength but low wet strength according to the present invention by use of a preferred hydroxyamidinoethylene-carbamylethylene polymer.

The resin was prepared by dissolving 5.0 gm. of an 80%–20% (molar ratio) acrylamide:acrylonitrile polymer (molecular weight 500,000) in 200 ml. of water, adding 0.655 gm. of hydroxylamine hydrochloride (equivalent to 64% of the nitrile groups present), adjusting the pH to 6.8 with dilute aqueous NaOH solution, and heating the mixture for 30 minutes at 90° C. The resulting polymer was substantially composed of carbamylethylene, hydroxyamidinoethylene and cyanoethylene linkages in approximately 8:1:1 molar ratio, and was diluted to 5% solids with water and cooled.

Dry strength paper containing the resin was made by standard laboratory procedure using 50:50 bleached sulfite:bleached hardwood kraft pulp. The pulp was diluted to 0.6% consistency, aliquots withdrawn, and the polymer solution added with and without alum as shown in the table, the alum when used being added before the polymer. After addition of the polymer the aliquots were gently stirred for 5 minutes and then sheeted on a Nash handsheet machine at 45–50 lb. basis weight (25" x 40"/500 ream). The sheets were drum dried for one minute at 250° F. and tested after conditioning at 73° C. and 50% relative humidity for 24 hours.

Results are as follows.

Run No.	Pulp Treatment		Pulp pH[2]	Paper			
	Percent Alum[1]	Percent Resin[1]		Tensile,[3] Lb./in.		Burst	
				Dry	Wet	Found,[4] Lb./in.	Percent Incr.
1	None	None	4.5	11.0	<0.6	16.8	-------
2	None	None	6.5	10.8	<0.6	16.6	-------
3	None	0.5	5.2	15.5	-------	24.9	[5] 48.0
4	None	0.5	7.0	15.3	-------	24.5	[6] 47.6
5	0.5	0.5	4.7	17.8	-------	28.2	[5] 68.0
6	0.5	None	6.5	12.4	0.4	19.1	-------
7	0.5	0.5	6.5	19.5	1.9	32.1	[7] 68.0

[1] On dry weight of fibers.
[2] During addition of polymer solution.
[3] By TAPPI method.
[4] Adjusted to 45 lb. basis weight (25" x 40"/500 ream).
[5] Over control (Run No. 1).
[6] Over control (Run No. 2).
[7] Over control (Run No. 6).

Example 2

The following illustrates the improved results obtained with rosin size when the size is supplied in conjunction with a linear polymer carrying hydroxyamidino groups. The papers were made according to the method of Example 1, wood rosin size and alum being added prior to the polymer. Results are as follows, the first three runs being controls.

Run No.	Pulp Treatment[1]			Pulp pH	Paper		
	Percent Alum	Percent Size	Percent Resin		Burst,[2] Lb./in.	Lactic Acid,[3] Sec.	Ink B.K.Y.,[4] Sec.
1	2.0	None	None	5.5	19.0	Inst.	Inst.
2	2.0	None	0.5	5.5	29.8	Inst.	Inst.
3	2.0	1.5	None	5.5	17.5	170	138
4	2.0	0.5	0.5	5.5	28.6	235	197
5	2.0	1.5	0.5	5.5	27.6	1245	363

[1] On dry weight of fibers.
[2] Corrected to a 45 lb. basis weight (25" x 40"/500 ream).
[3] Lactic acid resistance; Penescope test.
[4] Writing ink penetration resistance.

Example 3

The following illustrates the improvements in dry strength obtained by additional hydroxyamidinoethylene-carbamylethylene polymers. The general method of Example 1 was followed for preparation of the polymers and manufacture of the paper samples, 0.5% of polymer being added to the pulp samples in each instance.

Polymers 1–4 were prepared by copolymerizing acrylonitrile and acrylamide and then reacting with hydroxylamine to convert nitrile groups to the proportion of hydroxyamidino groups as shown in the table. Thus polymer No. 1 was prepared by copolymerizing acrylamide and acrylonitrile in 80:20 molar ratio and then reacting with hydroxylamine calculated as equivalent to 75% of the acrylonitrile.

Polymer 5 was prepared by copolymerizing acrylamide, acrylonitrile and vinyl acetate in 10:40:50 molar ratio and then reacting with hydroxylamine to convert 87% of the nitrile groups to hydroxyamidino groups.

Polymers 6–9 were prepared in similar manner except that in place of vinyl acetate there were respectively employed the ester of acrylic acid with polyethyleneoxide, the ester of acrylic acid with diethylaminoethanol, N,N-diethylacrylamide and p-vinyl benzonitrile.

Results are as follows.

Run No.	Linkages [1]					Pulp pH	Dry Burst,[2] Lb./in.
	Percent AOX	Percent AM	Percent CN	Other			
				Formula	Percent		
Control	No polymer added					5.5	18
1	15	80	5			5.5	31
2	30	50	20			5.5	29
3	70	20	10			5.5	30
4	90		10			5.5	29
5	35	30	5	$—CH_2CHOH—$	30	5.5	28
6	35	50	5	(3)	10	5.5	23
7	35	50	5	(4)	10	5.5	27
8	35	50	5	(5)	10	5.5	27
9	35	50	5	(6)	10	5.5	29

[1] AOX=hydroxyamidinoethylene; AM=carbamylethylene; CN=cyanoethylene.

[2] Corrected to 45 lb. basis weight (25" x 40"/500 ream).

[3] $—CH_2CH[COO(CH_2CH_2O)_{30}H]—$.

[4] $—CH_2CH[COOCH_2CH_2N(CH_2CH_3)]—$.

[5] $—CH_2CH[CON(CH_2CH_3)_2]—$.

[6] $—CH_2CH(C_6H_4CN)—$.

Example 4

The following illustrates the effect of the presence of alum and particular pH values on paper made in accordance with the present invention.

The handsheets were prepared in accordance with the general procedure of Example 1 except that the resin was prepared by copolymerizing acrylamide and acrylonitrile in 69.3:30.7 molar ratio and reacting with hydroxylamine stoichiometrically equivalent to the nitrile groups.

Results are as follows. The first four runs are controls.

Run No.	Pulp Treatment		Pulp pH [1]	Paper		
	Percent Alum [1]	Percent Resin [1]		Dry Tensile,[1] Lb./in.	Dry Burst,[1] Lb./in.	Fold, M.I.T.
1	0.5	None	4.7	12.0	18.3	11
2	0.5	None	6.5	12.3	18.9	11
3	2.0	None	4.7	12.5	19.3	13
4	2.0	None	6.5	13.0	20.2	14
5	0.5	0.55	3.5	16.9	27.6	38
6	0.5	0.55	4.7	18.5	31.0	75
7	0.5	0.55	6.0	18.3	30.0	80
8	0.5	0.55	6.5	18.6	30.9	66
9	0.5	1.1	4.7	20.4	34.2	124
10	2.0	0.55	4.7	18.5	30.0	61
11	2.0	0.55	6.0	18.0	30.1	72

[1] See footnotes to table of Example 1.

The results show that the process is insensitive to pH changes in the range of 3.5 to 6.5 and to the presence of excess alum.

I claim:

1. Paper of substantially improved dry strength but of low wet strength composed of a waterlaid web of cellulosic papermaking fibers bonded together by 0.1%–5%, based on the dry weight thereof, of a normally water-soluble ampholytic linear carbon chain vinyl polymer predominantly composed of recurring hydroxyamidinoethylene and carbamylethylene linkages, the ratio between said linkages being between about 1:100 and 10:1, said polymer having a molecular weight in excess of 100,000.

2. Paper according to claim 1 wherein the polymer consists of hydroxyamidinoethylene, carbamylethylene and cyanoethylene linkages.

3. Paper according to claim 1 wherein the ratio of hydroxyamidinoethylene to carbamylethylene linkages is between about 1:10 and 3:10.

4. Paper according to claim 1 wherein the polymer bonding the fibers is complexed with alum.

5. Sized paper of substantially improved dry strength but of low wet strength and of improved resistance to penetration by aqueous fluids composed of a waterlaid web of rosin sized cellulosic papermaking fibers bonded together by 0.1%–5%, based on the dry weight of said fibers, of a normally water-soluble ampholytic linear carbon chain vinyl polymer predominantly composed of recurring hydroxyamidinoethylene and carbamylethylene linkages, the ratio between said linkages being between about 1:100 and 10:1, said polymer having a molecular weight in excess of 100,000 and acting synergistically with said size to render said fibers resistant to penetration by aqueous fluids.

6. Process for the manufacture of paper of substantially improved dry strength but of low wet strength which comprises forming an aqueous suspension of papermaking cellulosic fibers, adding thereto between about 0.1% to 5%, based on the dry weight of the fibers, of a water-soluble ampholytic liner carbon chain vinyl polymer substantially composed of recurring hydroxyamidinoethylene and carbamylethylene linkages, the ratio between said linkages being between about 1:100 and 10:1, said polymer having a molecular weight in excess of 100,000, whereby said polymer is adsorbed on said fibers, sheeting said fibers to form a cellulosic web, and heating said web until dry at a temperature between 190° F. and 250° F.

7. A process according to claim 6 wherein the cellulosic fibers in the suspension to which the polymer is added are rosin sized.

8. A process according to claim 6 wherein the sus-

pension during addition of the polymer contains between about 0.1% and 2% of alum based on the dry weight of the fibers.

9. A process according to claim 6 wherein the pH of the suspension during addition of the polymer is between 4.5 and 6.5.

10. A process according to claim 6 wherein the molecular weight of the polymer is between 500,000 and 5,000,000.

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