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DRAINAGE IMPROVEMENT IN PAPER PULP SUSPENSIONS CONTAINING LIGNIN RESIDUES

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ABSTRACT OF THE DISCLOSURE

Drainage is improved in a cellulosic pulp suspension containing soluble lignin residues by the addition to the suspension of a high molecular weight water-soluble anionic polymeric polyelectrolyte and alum in a quantity greater than that normally used.

BACKGROUND OF THE INVENTION

The invention is an improvement in the manufacture of paper, paperboard, or other such cellulosic fiber sheets generically referred to as paper from aqueous cellulosic fiber suspensions containing lignin residues, the so-called black liquor solids.

The term "black liquor solids" is used herein to refer to lignin residues characteristically present in some papermaking systems. Black liquor is the liquor containing residues formed by cleavage and solubilization of lignin during the cooking of pulpwood. In the neutral sulfite semi-chemical process, the lignin residues in the black liquor are primarily lignosulfonates. In the manufacture of corrugated medium from neutral sulfite semi-chemical pulp, the black liquor solids are usually present in concentrations of 25–100 percent based on the fiber content. In the manufacture of kraft linerboard, the black liquor solids are present in lower concentrations of the order of 2–10 percent of the weight of fiber. These solids are largely substituted sodium phenolates. The improvement concerns specifically the use in such suspensions of a combination of aluminum ion and an anionic water-soluble high molecular weight acrylic polymer.

In most papermaking systems, whether black liquor solids are present or not, drainage of the pulp suspension in forming the paper web is accomplished by filtration in the table roll or foil section of the Fourdrinier wire using a relatively low pressure drop across the wet mat. This is followed by a vacuum filtration operation using a much higher pressure drop. The well-known Canadian Standard Freeness Test measurement provides a convenient and accurate indication of the drainage rate for a particular suspension in the table roll or foil section of the wire.

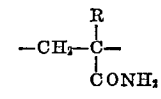
It is known to use alum and anionic water-soluble high molecular weight vinyl polymers to promote drainage and filler retention in paper systems which are free or essentially free of lignin residues, otherwise known as black liquor solids. In paper systems containing black liquor solids, it is found that alum-polymer combinations show apparently favorable results by the Canadian Standard Freeness Test, but actually hinder drainage in practice and cannot be used. Apparently the alum-polymer combinations allow good drainage in the low pressure filtration operation, but hinder it in the vacuum filtration operation.

Cationic polymers such as N-aminoalkylated polyacrylamides, commonly used in paper pulp systems not containing black liquor solids, can also be employed to accelerate drainage in paper systems containing black liquor solids, but the presence of these solids makes necessary the use of uneconomic amounts of polymer.

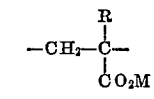
SUMMARY OF THE INVENTION

It has now been found that drainage under vacuum filtration of aqueous cellulosic pulp suspensions containing substantial amounts of lignin residues is significantly improved when there is incorporated into such suspensions prior to formation of the paper web about 0.02–0.1 percent based on the weight of dry cellulosic pulp of a water-soluble anionic polymeric polyelectrolyte and a water-soluble aluminum compound sufficient to improve drainage of the pulp. The quantity of aluminum compound is in excess of that normally used in these paper pulp suspensions. Illustrative anionic polyelectrolytes are those of monomers containing acidic groups in their molecular structure such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid styrenesulfonic acid, and other similar monomers. Also included are the water-soluble copolymers of these with other vinyl monomers such as acrylamide, methacrylamide, acrylonitrile, vinyl acetate, vinyl chloride, alkyl methacrylates, oxazolidinone, pyrrolidinone, and so on. Also useful for this use are water-soluble homopolymers and copolymers of the sulfoalkyl acrylates and carboxyalkyl acrylates such as sodium sulfoethyl acrylate and sodium carboxyalkyl acrylate. Still other such polymers known to be useful anionic flocculants include carboxyalkyl cellulose derivatives and similar derivatives of other polysaccharides such as starch. Preferably, the polymer is of relatively high molecular weight, i.e., at least about one million.

Preferred polymers are those of which the molecular structure is essentially composed of carbamoylalkylene units of the formula



and carboxyalkylene units of the formula



wherein the carboxyalkylene units are at least about 20% and can constitute all of the total monomer units present, and M is hydrogen or a water-soluble salt forming cation such as ammonium, alkaline earth metal, or alkali metal, preferably sodium, R is hydrogen or a methyl radical.

DETAILED DESCRIPTION

The invention is applicable to any of the so-called black-liquor systems wherein significant quantities of lignin residues are present in the pulp suspension. Specifically, these systems include kraft linerboard suspensions of unbleached kraft pulp where the black liquor solids characteristically are present in the headbox pulp suspensions in amounts of about 2–10 percent of the weight of fiber, and also neutral sulfite semi-chemical pulp suspensions used for making the corrugated paperboard which with the linerboard makes up the familiar sandwich construction of shipping containers, which sus-

pensions in the headbox may contain about 25–100 percent of black liquor solids or lignin residues based on the fiber content.

Kraft linerboard suspensions ordinarily are formed at about pH 5.5–7.5, usually at about pH 6–6.5, with about 0.5–1 percent fiber content and usually contain some rosin sizing in a quantity of about 0.1–0.5 percent based on the weight of fiber. About 0.5–1 percent of alum based on fiber content is conventionally used in such pulp suspensions. In the practice of the present invention, polymer is also added as specified above and ordinarily an additional quantity of alum as further defined later.

Neutral sulfite semi-chemical pulp suspensions normally are formed at a higher pH, for example, about 7–9, but contain about the same proportion of fiber with a considerably higher proportion of lignin residues as previously described. These suspensions are usually made up with no rosin sizing and no alum. In the process of this invention, however, both alum and polymer are added to such pulp suspensions.

The polymer used in the invention can be prepared by any conventional process of polymerization or copolymerization. When both carbamoylalkylene and carboxyalkylene moieties are present in the polymer structure, the polymerization in this case can be combined with a hydrolysis step wherein carbamoyl groups in a polymer structure are converted to carboxygroups by reaction with a base such as sodium hydroxide or sodium carbonate. Thus, a polyacrylamide or polymethacrylamide can be converted to a polymer having the same structure as that obtained by copolymerizing acrylamide and acrylic acid or the corresponding methacrylic monomers. As a practical matter, in order to make a polymer having a relatively high proportion of acid moieties in its structure, it is most convenient to copolymerize the amide and acid monomers in the desired proportion. In any case, polymers of high molecular weight are used, i.e., those having an average molecular weight of at least 1–10 million.

Preferably, such a polymer structure contains at least about 25 percent of carboxyalkylene moieties based on the total monomer units. With an increasing proportion of carboxy groups, less additional alum or other source of aluminum is required to obtain improved drainage. The carboxy groups in the polymer as used are ordinarily in the form of their sodium salt. The same is true of the acid groups in other polymers useful in this invention.

Performance is also sensitive to other variables such as changes in pH and the amount of black liquor solids in the suspension. Generally, more aluminum compound is needed for optimum results at higher pH and higher concentrations of black liquor solids. For example, in kraft linerboard systems containing 2–5 percent of lignin residues, the minimum amount of alum required for good results may increase from about 0.5–1 percent at pH 5 to about 5 percent at pH 7 while an increase in black liquor solids to 8 or 10 percent may well require that the quantity of alum be increased by at least half. In general, alum is used in this process in a quantity of about 0.2 to about 10 percent based on fiber content. Preferably, about 1–5 percent of alum or its equivalent is employed.

Aluminum, as suggested above, is normally supplied in papermaking process as alum, by which is meant hydrated aluminum sulfate. Other water-soluble aluminum salts can be employed in equivalent amounts, for example, aluminum chloride, other alums, or sodium aluminate to provide the same concentration of alumina.

The term "alum" herein is used generically to mean aluminum sulfate hydrated with about eighteen molecules of water or its equivalent in aluminum content of another water-soluble aluminum compound.

Calcium chloride or other such water-soluble polyvalent metal salt can be used in place of up to about half of the alum. Usually, several pounds of calcium chloride are required to replace a pound of alum and still provide the same results.

In the process of the invention, the polymer and the alum can be dissolved in the pulp suspension at any appropriate point prior to formation of the paper web. They are preferably added as dilute water solutions. In a system where sodium aluminate is used as the source of aluminum, a combination of the aluminate and the polymer in pre-determined proportions may be dissolved in water and added together or a dry blend of the two materials can also be used. When a sodium aluminate-polymer combination is employed, it is important that the acid groups in the polymer be in water-soluble salt form, usually the sodium salt, and that the polymer be dissolved in the presence of sodium aluminate. Advantageously, such polymer-sodium aluminate blends contain about 1 to 4 parts by weight of anionic polymeric polyelectrolyte for each 1 to about 30 parts of aluminate. Preferably, compositions of this kind contain one part of polymer to from 1 to about 20 parts of aluminate.

The polymers used in the following examples had average molecular weights of at least one million, generally in the range of 5–50 million as calculated from intrinsic viscosity measurements. Usually, both the polymers and the aluminum compound were added to the pulp suspensions as described in the form of dilute aqueous solutions, but dry materials were also used.

Example 1

A simulated kraft linerboard pulp system was made up by beating 23 liters of 1.5 percent unbleached kraft pulp suspension with a laboratory beater until a Canadian Standard Freeness of about 400 ml. was reached. This was diluted to one percent fiber content with water and 10% of dissolved black liquor solids (solid lignin residues) based on the weight of fiber was added. From the resulting suspension, 300 ml. samples were withdrawn, diluted to 1000 ml. with water, and the pH was adjusted to the desired level by adding 1 N HCl. Alum was added in a pre-determined amount, the suspension was stirred for two minutes, and the pH was then re-adjusted to its original level by appropriate addition of 1 N NaOH. The desired amount of anionic polymer was mixed with the suspension (as a 0.05% aqueous polymer solution) and the suspension was poured into a vacuum filtration apparatus on which a constant vacuum of 500 mm. of mercury was maintained. The time in seconds required to obtain 900 ml. of filtrate was then noted.

In this experiment, filtrations were run as described above at pH 5, 6 and 7 using various quantities of alum and 0.05% based on the weight of fiber of a copolymer of acrylamide and acrylic acid or corresponding partially hydrolyzed polyacrylamide having an average molecular weight of the order of five million and containing from ten to ninety mole percent of acrylic acid moieties, sodium salt form, in its molecular structure. Results are listed in Tables 1–3.

TABLE 1

[pH=5.0]

Percent alum	Mole percent acrylic acid in polymer—				
	10	30	50	70	90
0.15					171
0.25				187	105
0.35				99	116
0.5			240	120	132
0.6			94	127	
0.75		383	104	128	
0.9			117		
1.0		148			
1.1		130			
1.25		119			
1.5		131			
1.75	231				
2.0	94				
2.25	87				
2.5	77				
3.0	80				

NOTE.—Controls: No polymer, no alum—150 seconds; no polymer, 0.75% alum—151 seconds.

TABLE 2

[pH=6.0]

Percent alum	Mole percent acrylic acid in polymer— 10	30	50	70	90
0.15					150
0.25				147	113
0.35			237	103	
0.5			122	99	120
0.6			103	113	
0.75			120		125
1.0					133
1.25		247			
1.5		172			145
2.0	>1,000	150			
2.25		99			138
2.5		90			
3.0	239	96			137
3.25	72				
3.5	67				
3.75		91			137
4.0	72				
5.0	69				

NOTE.—Controls: No polymer, no alum—160 seconds; no polymer 1% alum—170 seconds; no polymer, 3.75% alum—190 seconds.

TABLE 3

[pH=7.0]

Percent alum	Mole percent acrylic acid in polymer— 10	30	50	70	90
0					235
0.25					190
0.35					125
0.5				219	115
0.6				135	
0.75				109	115
0.9				119	
1.0					112
1.5			293		
2.5			189		
3.5			139		
4.5	>1,000	156			
5.0			101		
6.0	130	102	85		
7.5	66	67	58		
9.0	66	64			

NOTE.—Controls: No polymer, no alum—150 seconds.

Example 2

A pulp suspension was made up as described in Example 1 with 0.3% fiber content, 10% black liquor solids, and a constant 3% alum loading. Vacuum filtration tests were run as in the above example after the pH was adjusted to the desired value and 0.05% of acrylic acid-acrylamide copolymer of defined composition as described in Example 1 was added. The filtration times in seconds required to collect 900 ml. of filtrate are listed in the table. Control runs with no polymer added were made for comparison.

FILTRATION TIME, SECONDS

pH	No polymer	Mole percent acrylic acid moieties in polymer 10	20	25	30	50	70	90
5.0	203	115	150	160	166	180	174	166
6.0	240	183	80	78	73	80	108	125
7.0	243	>1,000	>1,000	>1,000	379	63	79	92
8.0	240				>1,000	>1,000	245	129

Example 3

Following the procedure of Example 1, a kraft pulp suspension was made up to pH 6.2 and filtrations were run as before to show the effect of black liquor solids concentration at different alum loadings. A partially hydrolyzed polyacrylamide of about 5 million average molecular weight having 20–25 percent of the initial carboxamide groups hydrolyzed to sodium carboxylate groups was used at a level of 0.05% concentration based on the fiber content. Times listed are in seconds required to collect the total filtrate from a liter sample at 500 mm Hg vacuum.

Percent alum	Percent black liquor solids	Filtration time
0 (no polymer)	10	282
2.25	10	1,110
3.0	10	270
3.75	10	192
3.75 (no polymer)	5	288
1.5	5	552
2.25	5	162
3.0	5	162
3.75	5	138

EXAMPLE 4

A kraft linerboard pulp suspension was prepared as described in Example 1 to contain 0.3 percent pulp fiber and ten percent black liquor solids based on the fiber content. The suspension was adjusted to the desired pH value and alum and 0.05% polymer were added as previously described. In this case, the anionic polymer was sodium polystyrenesulfonate having an average molecular weight of about 5–10 million. Filtration times for 900 ml. of filtrate were determined under conditions previously described.

Percent polymer	Percent alum	pH	Time, seconds
0	0	6.0	196
	3	6.0	207
0.05	1.5	6.0	>1,000
	2.25	6.0	280
	3	6.0	133
	3.75	6.0	120
	3	5.0	157

EXAMPLE 5

In the manner shown in Example 1, a kraft linerboard suspension was prepared containing 10% black liquor solids based on the 0.3% fiber content and 0.05% of the ploymer described in Example 3. Experiments were performed with various quantities of alum and combinations of alum and calcium chloride at pH 6.0. Calcium chloride was added after the pH was adjusted following addition of alum. Filtration times of 900 ml. filtrate were determined as before.

Percent alum	Percent $CaCl_2$	Filtration time, seconds
0[1]	0	119
	1.7	108
1.0	0	351
1.25	0	102
1.5	0	92
1.75	0	78
1.0	1.7	119
1.25	1.7	84
1.5	1.7	76
1.75	1.7	71

[1] No polymer was present.

EXAMPLE 6

A typical kraft linerboard pulp suspension had the following composition:

	Percent
Unbleached kraft fiber	0.58
Black liquor solids [1]	6.2
Alum [1]	0.5
Rosin size [1]	0.13

[1] Based on fiber.

Four 550 ml. samples of the suspension were diluted to one liter with water, the pH of each was adjusted to one liter with water, the pH of each was adjusted with NaOH or HCl as desired, and a dry, blended mixture of five parts by weight sodium aluminate to one part of the partially hydrolyzed acrylamide polymer of Example 3 was added to two of the suspension samples in a quantity to provide 0.05% of polymer based on the fiber content. The samples were then suction filtered using 20 inches Hg vacuum and the times in seconds required to obtain a measured quantity of filtrate was noted in each case. The results are summarized in the following table.

Treatment	Final pH	Time for volume of filtrate, ml. 500	700	900
Control	7.0	16	34	60
	6.0	16	32	55
Polymer plus $NaAlO_2$	7.0	7	13	23
	6.0	10	19	34

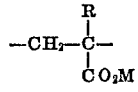
We claim:

1. In a papermaking process wherein an aqueous suspension of cellulosic pulp containing a substantial quantity of lignin residues is produced and a paper web is formed therefrom, the improvement wherein there is dissolved in the suspension prior to web formation about 0.02–0.1 percent based on the weight of dry cellulosic pulp of a high molecular weight water-soluble anionic polymeric polyelectrolyte plus a drainage-improving quantity of a water-soluble aluminum compound.

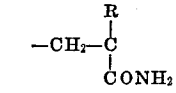
2. The process of claim 1 wherein the polymer is a polystyrenesulfonate.

3. The process of claim 1 wherein calcium chloride is substituted for a portion of the aluminum compound in an amount of up to about half of the aluminum compound.

4. The process of claim 1 wherein the polymer is one in which the molecular structure is composed essentially of carboxyalkylene units of the formula



and carbamoylalkylene units of the formula



in which structure the carboxyalkylene units are at least about 25 percent of the total units present and in which each R is hydrogen or a methyl radical and M is hydrogen or a water-soluble salt-forming cation.

5. The process of claim 4 wherein the polymer is added to the pulp suspension in combination with sodium aluminate.

6. The process of claim 4 wherein the pulp suspension is an unbleached kraft linerboard suspension containing about 2–10 percent of lignin residues and the suspension has a pH of about 5.5–7.5.

7. The process of claim 6 wherein R is hydrogen in the carboxyalkylene and carbamoylalkylene units of the polymer structure.

8. The process of claim 7 wherein the water-soluble aluminum compound is alum and the alum is present in a quantity of about 0.2–10 percent based on the weight of cellulosic pulp.

9. The process of claim 8 wherein about 1–5 percent of alum is present.

10. The process of claim 4 wherein the pulp suspension is a neutral sulfite semi-chemical pulp suspension containing about 25–100 percent of lignin residues and the suspension has a pH of about 7–9.

11. The process of claim 10 wherein R is hydrogen in the carboxyalkylene and carbamoylalkylene units of the polymer structure.

12. The process of claim 10 wherein the water-soluble aluminum compound is alum and the alum is present in a quantity of about 0.1–10 percent based on the weight of cellulosic pulp.

13. The process of claim 10 wherein about 1–5 percent of alum is present.

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