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(71) Applicant: **CALGON CORPORATION**  
**Pittsburgh, Pennsylvania 15205 (US)**

(72) Inventors:  
• **Elliot, David L.**  
**Imperial, Pennsylvania 15126 (US)**

• **Falcione, Ronald J.**  
**Canonsburg, Pennsylvania 15317 (US)**  
• **Henderson, Kenneth F.**  
**Pittsburg, Pennsylvania 15241 (US)**

(74) Representative: **McCormack, Derek James**  
**English China Clays plc**  
**1015 Arlington Business Park**  
**Theale**  
**Reading, Berkshire RG7 4SA (GB)**

(54) **Paper furnish composition and process for making tissue, newsprint, paper or paperboard**

(57) An improved paper furnish composition comprising an aqueous cellulosic furnish, a high molecular weight anionic polymer, and a modified lignin wherein the ratio of the anionic polymer to the modified lignin is from about 10:1 to 1:10 on an active basis is disclosed. A process employing this composition for making tissue, newsprint, paper or paperboard having improved drainage, retention, or formation and combinations thereof which enhance the pressing and drying operations of a paper machine is also provided. Preferably, the anionic polymer is added to the furnish prior to a shear stage, and the modified lignin is added subsequently.

**EP 0 722 011 A1**

**Description**BACKGROUND OF THE INVENTION5 1. Field of the Invention

This invention relates to a composition comprising an aqueous cellulosic furnish, anionic polymer and a modified lignin and methods using the composition for making tissue, newsprint, paper or paperboard having improved properties in the areas of drainage, retention and formation, which enhance the pressing and drying operations of a paper  
10 machine.

2. Brief Description of the Background Art

In the production of tissue, newsprint, paper or paperboard from a dilute aqueous cellulosic furnish improvements  
15 in retention and drainage and in the formation properties of the final tissue, newsprint, paper or paperboard sheet are particularly desirable. Further, it is desirable to improve the pressing and drying operations in the production of tissue, newsprint, paper or paperboard. It is well known by those skilled in the art that these parameters are frequently in conflict with each other. For example, if the cellulosic fibers of the aqueous cellulosic furnish are flocculated effectively to larger  
20 flocs, retention of, for example, fiber fines and filler is generally good and can result in a porous structure yielding generally good drainage; however, formation is poor. In this light, conventional practice has resulted in those skilled in the art selecting one or more additives to improve the production of tissue, newsprint, paper or paperboard according to the parameters that are most important to achieve. Alternatively, if the cellulosic fibers are flocculated to a lesser degree, drainage and retention are less satisfactory; however, formation is improved. Further, drainage and retention are often  
25 in conflict with each other when, for example, increased production of paper, tissue, newsprint, or paperboard is desired over the need for retention of, such as for example, fillers and the like. Improvements in the areas of drainage, retention and formation enhance the pressing and drying operations in the production of tissue, newsprint, paper or paperboard.

Retention is believed to be a function of different mechanisms such as filtration by mechanical entrainment, electrostatic attraction and bridging between aqueous cellulosic fibers and filler. Because both cellulose and many common fillers are electronegative, they are mutually repellant and, in the absence of a retention aid, the only factor tending to  
30 enhance retention is mechanical entrainment.

Drainage relates to the rate at which free water is released from a sheet as it is being formed. Thus, it will be appreciated that drainage aids improve the overall efficiency of dewatering in the production of tissue, newsprint, paper or paperboard.

Formation relates to the formation of the tissue, newsprint, paper or paperboard sheet produced from the papermaking process. Formation is generally evaluated by the variance in light transmission within a paper sheet. A high variance is indicative of poor formation. It is generally well known by those skilled in the art that as the retention level increases, the level of formation generally decreases from good formation to poor formation.

A variety of compositions and processes have been proposed to improve retention, drainage, or formation to improve the papermaking process, but none of these teach or suggest the composition and process of the instant invention which results in producing tissue, newsprint, paper or paperboard having improved drainage, retention, and formation properties.  
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U. S. Patent No. 4,347,100 (Brucato) discloses a method of producing paper having improved bursting strength from mechanical or thermomechanical pulp comprising defibering wet wood by mechanical attrition to form mechanical or thermomechanical pulp, processing the pulp to form a furnish, incorporating into the pulp at an elevated temperature and pressure an anionic organic polyelectrolyte or polymer to improve bursting strength, and adding to the furnish a  
45 cationic organic polyelectrolyte or polymer. The patent states that the anionic organic polyelectrolyte or polymer causes dispersion of lignin and retards deposition of lignin to improve the bursting strength. This patent discloses that the anionic polyelectrolyte or polymer must be incorporated into the pulp by cooking at elevated temperature and pressure before or during the refining or defibering stage to achieve the desired end result of paper having improved bursting strength. This patent states that the anionic organic polyelectrolyte or polymer is a polymeric sulfonate.  
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TAPPI, Papermakers Conference Proceedings, Book 1, pp. 115-186, (Atlanta, Georgia - April 18-21, 1993) discloses microparticle systems such as for example, a system having a cationic starch or cationic polyacrylamide or anionic polymers and an anionic silica colloid or bentonite or alumina sol for improving dewatering, retention, formation and dry strength.

It will be appreciated by those skilled in the art that the above mentioned background technical publications do not teach or suggest the addition of lignin or modified lignin to paper furnishes having an anionic polymer component for producing an aqueous cellulosic furnish having improved drainage, retention and formation properties. Therefore, it will be understood by those skilled in the art that applicants have discovered unexpectedly that the composition and process of the instant invention comprising adding a modified lignin to an aqueous cellulosic furnish having a high molecular  
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weight anionic polymer component results in producing tissue, newsprint, paper or paperboard having improved drainage, retention, formation, pressing and drying properties that are superior to results of others previously achieved.

In spite of this background material, there remains a very real and substantial need for a composition and process for making improved tissue, newsprint, paper or paperboard in the areas of drainage, retention, or formation, and combinations thereof, which enhance the pressing and drying operations of a paper machine.

### SUMMARY OF THE INVENTION

The present invention has met the above-described needs. The present invention provides a process in which tissue, newsprint, paper or paperboard having unexpectedly improved properties is made by forming an aqueous cellulosic paper furnish, adding to the furnish an effective amount, based on the dry weight of the solids of the furnish, of (A) a high molecular weight anionic polymer and (B) a modified lignin, draining the slurry to form a sheet and drying the sheet. The weight ratio of the anionic polymer (A) to the modified lignin (B) is from about 10:1 to 1:10, on an active basis, more preferably from about 5:1 to 1:5, and most preferably from about 3:1 to 1:3.

In a preferred embodiment of this invention, the process as described herein is provided wherein the modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidized lignin, and salts thereof. In another preferred embodiment of this invention, the process wherein the sulfonated lignin has a degree of sulfonation of from about 0.1 to 10 moles of sulfonic acid groups per 1000 unit weight of the lignin is included.

In yet another embodiment of this invention, tissue, newsprint, paper or paperboard produced by the process of this invention is provided wherein the tissue, newsprint, paper or paperboard has improved properties in the areas of retention, drainage or formation, and combinations thereof, which enhance the areas of pressing and drying.

Another embodiment of this invention provides a process in which paper or paperboard is made by forming an aqueous cellulosic paper furnish comprising subjecting the furnish to one or more shear stages, adding to the furnish prior to at least one of the shear stages a high molecular weight anionic polymer (A), adding to the furnish subsequent to the addition of the anionic polymer and at least one shear stage subsequent there to, a modified lignin (B), draining the furnish to form a sheet and drying the sheet. The weight ratio of the anionic polymer (A) to the modified lignin (B) is from about 10:1 to 1:10, on an active basis, more preferably from about 5:1 to 1:5, and most preferably from about 3:1 to 1:3.

Another embodiment of this invention provides a composition comprising (a) an aqueous cellulosic furnish, (b) a high molecular weight anionic polymer, and (c) a modified lignin wherein the ratio of the anionic polymer to the modified lignin is from about 10:1 to 1:10, on an active basis, more preferably from about 5:1 to 1:5 and most preferably from about 3:1 to 1:3.

In another embodiment of this invention, tissue, newsprint, paper or paperboard is provided comprising the composition of this invention.

### DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a process in which tissue, newsprint, paper or paperboard having improved properties is made and the composition for improving drainage, retention, or formation, and combinations thereof which enhances pressing or drying in the manufacture of tissue, newsprint, paper or paperboard.

As used herein, the term "furnish" refers to all tissue, newsprint, paper and paperboard furnishes based on, for example, but not limited to, mechanical pulp, semi-bleached kraft pulp, recycled pulp, unbleached kraft pulp and/or unbleached sulfite pulp.

As used herein, the term "active basis" means a concentration of additive based on the solids in the stock solution.

As used herein, the term "paper" includes, but is not limited to, paper, newsprint, tissue, or paperboard.

As used herein, the term "effective amount" refers to that amount of the composition necessary to bring about a desired result, such as, for example, the amount needed to improve drainage, retention, or formation, and combinations thereof, which enhances pressing or drying operations in the manufacture of paper or paperboard.

The present invention provides an improved paper furnish composition comprising (a) an aqueous cellulosic furnish, (b) a high molecular weight anionic polymer, and (c) a modified lignin, wherein the ratio of the anionic polymer to the modified lignin is from about 10:1 to 1:10, on an active basis, wherein the improved paper furnish composition exhibits improved drainage, retention and formation and enhanced pressing and drying with respect to the aqueous cellulosic furnish. The modified lignin used in the instant invention can be derived from the kraft pulping process and may be, for example, but not limited to, fractionated lignins in terms of molecular weight, purified or may be used in either the protonated or salt forms. In a preferred embodiment of this invention, the modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidized lignin and salts thereof.

The modified lignin used in the instant invention can be derived from the sulfite pulping process for example, but not limited to, a lignin adduct copolymerized with phenol and formaldehyde resulting in a modified lignin having a weight average molecular weight greater than about 30,000 such as for example Dynasperse A commercially available from Lignotech USA, Inc., Greenwich, CT. Further, the modified lignin used in the instant invention can be derived from a

condensation reaction of a sulfonated lignin and formaldehyde resulting in higher weight average molecular weights greater than above 10,000, such as for example REAX-905 commercially available from Westvaco Chemical Division (Charleston Heights, South Carolina).

In a most preferred embodiment of this invention, the composition as described herein includes a sulfonated lignin that has a degree of sulfonation of from about 0.1 to 10 moles of sulfonic acid groups per 1000 unit weight of the lignin.

In a preferred embodiment of this invention, the composition as described herein includes wherein the sulfonated lignin has a weight average molecular weight of greater than about 2,500, more preferably greater than about 10,000, and most preferably greater than about 30,000.

The composition of the instant invention, as described herein, preferably includes wherein the weight ratio of the anionic polymer to the modified lignin is from about 5:1 to 1:5 and most preferably is from about 3:1 to 1:3.

In another embodiment of this invention, the anionic polymer of the instant composition is derived from at least one anionic monomer selected from the group consisting of an 2-acrylamido-2-methylpropanesulfonic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, styrene sulfonic acid, vinyl sulfonic acid, vinyl lactic acid, allyl sulfonic acid, alkali metal salts of carboxylic acids, and combination thereof.

It will be appreciated by those skilled in the art that anionic monomers such as, for example, polymeric sulfonates and polymeric carboxylates are commercially available as the water soluble salts of the corresponding sulfonic acids and acrylic acid polymers and copolymers, respectively. Copolymers, terpolymers, etc., such as, for example, copolymers comprising acrylic acid and acrylamide may be employed as the anionic polymer component of the composition of the instant invention. In a preferred embodiment of this invention, the anionic polymer is a copolymer derived from at least one of the hereinbefore mentioned anionic monomers and of at least one of a nonionic monomer selected from the group consisting of acrylamide, methacrylamide, diacetone acrylamide, and N,N-dimethyl acrylamide, wherein the ratio of the anionic monomer to the nonionic monomer is from about 99:1 to 1:99. Preferably, the weight ratio of the anionic monomer to the nonionic monomer is from about 3:97 to 60:40 and most preferably is from about 5:95 to 30:70. It will be appreciated by those skilled in the art that the ratio of mer units in such copolymers generally is determined by the quantity of anionic units necessary in the instant composition to impart the desired drainage, retention, and formation, or combinations thereof, for enhancing the pressing or drying operation in the manufacture of a particular tissue, newsprint, paper or paperboard. Further, additional anionic mer units may be present.

It will be understood by those skilled in the art that the anionic polymer component and the modified lignin component of the composition of this invention, as described herein, are water soluble or water dispersible.

It will be appreciated by those skilled in the art that when employing diacetone acrylamide as the nonionic monomer, it is preferable to employ less than about 35 weight percent of diacetone acrylamide for achieving adequate water solubility. It will be understood that employing more than 35 weight percent of diacetone acrylamide results in reduced water solubility.

An effective amount of the composition of the instant invention should be employed. It will be appreciated by those skilled in the art that the dosage of the composition added to the aqueous cellulosic furnish being treated is dependent on the degree of retention, drainage and formation desired. The anionic polymer and the modified lignin are each present in an amount of at least about 0.1 pounds per ton (0.004 per cent by weight) based on the dry weight of solids in the aqueous cellulosic furnish.

The high molecular weight anionic polymer component of the instant composition has a weight average molecular weight above about 300,000 and preferably above about 1,000,000. Most preferably, the high molecular weight anionic polymer component of the instant composition has a weight average molecular weight above about 2,000,000.

A preferred embodiment of this invention provides a composition, as hereinbefore described, wherein the anionic polymer is a copolymer derived from sodium acrylate and acrylamide. Preferably, the composition of the instant invention, as hereinbefore described, includes wherein the anionic polymer is a copolymer that is a 25 weight % active acrylamide sodium acrylate comprising from about 5 to 30% by weight sodium acrylate and from about 95 to 70% by weight acrylamide.

The composition of the instant invention can generally be successfully added to aqueous cellulosic furnishes over the entire pH range customarily employed in the papermaking process. Preferably, the composition of the instant invention is added to aqueous cellulosic furnishes having a pH from about 3 to 10. Therefore, it will be appreciated by those skilled in the art that the composition of the instant invention may be added to aqueous cellulosic paper furnishes that are acid, alkaline, or neutral in character. It will be understood by those skilled in the art that generally an acid furnish has a pH range from about 3.0 to 5.5, an alkaline furnish has a pH range from about 7.0 to greater than about 10.0, and a neutral furnish has a pH range of from about 5.5 to 7.0.

In another embodiment of this invention, a process is provided for in which tissue, newsprint, paper or paperboard is made by forming an aqueous cellulosic furnish having improved properties in the areas of drainage, retention and formation which comprises adding to the furnish an effective amount, based on the dry weight of the solids of the furnish, of (A) a high molecular weight anionic polymer, as hereinbefore described, and (B) a modified lignin, as hereinbefore described, draining the furnish to form a sheet and drying the sheet, wherein the weight ratio of the anionic polymer (A) to the modified lignin (B) is from about 10:1 to 1:10, on an active basis, preferably from about 5:1 to 1:5, and most pref-

erably about 3:1 to 1:3. In another embodiment of the instant invention, the process, as hereinbefore described, includes wherein the modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidized lignin and salts thereof. Preferably, the process includes wherein the sulfonated lignin has a degree of sulfonation of from about 0.1 to 10 moles of sulfonic acid groups per 1000 unit weight of the lignin.

5 In another embodiment of this invention, the process, as hereinbefore described, includes wherein the sulfonated lignin has a weight average molecular weight greater than about 2,500, preferably greater than about 10,000, and most preferably greater than about 30,000.

10 In a further embodiment of this invention the process includes wherein the anionic polymer is derived from at least one anionic monomer, as hereinbefore described. More preferably the process of this invention, as hereinbefore described includes wherein the anionic polymer is a copolymer derived from at least one of the anionic monomers and of at least one of the nonionic monomers as hereinbefore described. The instant process includes wherein the weight ratio of the anionic monomer to the nonionic monomer is from about 99:1 to 1:99, preferably from about 3:97 to 60:40, and most preferably from about 5:95 to 30:70.

15 The process of the instant invention includes adding an effective amount of the composition to the aqueous cellulosic paper furnish. It will be appreciated by those skilled in the art that the dosage of the composition added to the aqueous cellulosic paper furnish is dependent on the drainage, retention, formation, pressing and drying parameters desired. At least about 0.1 pounds per ton of the anionic polymer should be added to the furnish based on the dry weight of solids in the furnish. The instant process includes wherein at least about 0.1 pounds of the modified lignin is added to the furnish based on the dry weight of solids in the furnish.

20 It is believed that the pH of the aqueous cellulosic paper furnish is unimportant as the instant composition is effective in treating aqueous cellulosic paper furnishes having a wide range of alkaline, neutral and acidic pH's. Preferably, the process of the instant invention includes wherein the aqueous cellulosic paper furnish has a pH from about 3 to 10.

25 In another embodiment of the instant invention, a process is provided in which tissue, newsprint, paper or paperboard is made by forming an aqueous cellulosic paper furnish comprising subjecting the furnish to one or more shear stages, adding to the furnish prior to at least one of the shear stages a high molecular weight anionic polymer, as hereinbefore described, adding to the furnish subsequent to the addition of the anionic polymer and at least one shear stage subsequent thereto, a modified lignin, as hereinbefore described, draining the furnish to form a sheet and drying the sheet, wherein the weight ratio of the anionic polymer to the modified lignin is from about 10:1 to 1:10, on an active basis, preferably from about 5:1 to 1:5, and most preferably from about 3:1 to 1:3. A further embodiment of the instant invention includes a process for making tissue, newsprint, paper or paperboard, as described herein, including after draining the furnish to form the sheet, pressing the sheet and then drying the sheet.

30 A further embodiment of the instant invention provides a process, as hereinbefore described, including the anionic polymer derived from at least one anionic monomer, as hereinbefore described, and combinations thereof. Preferably, the instant invention includes the process wherein the anionic polymer is a copolymer derived from at least one of the anionic monomers, as hereinbefore described, and of at least one of the nonionic monomers, as hereinbefore described. The weight ratio of the anionic monomer to the nonionic monomer is from about 99:1 to 1:99.

35 Another embodiment of this invention includes tissue, newsprint, paper or paperboard produced by the process of the instant invention, as hereinbefore described, wherein the tissue, newsprint, paper or paperboard has improved properties in the areas of retention, drainage, or formation and combinations thereof.

40 It will be appreciated by those skilled in the art that the composition and process of this invention may be employed in conjunction with other additives used during the manufacture of tissue, newsprint, paper or paperboard such as, but not limited to, fillers, pigments, binders, and strength aids. Further, for example, but not limited to, the improved aqueous cellulosic paper furnish of the instant invention includes one or more of the following size, calcium carbonate, starch, clay, alum, resin titanium dioxide and broke.

45 The anionic polymers of the instant composition may be prepared using any conventional polymerization technique that is well known by those skilled in the art.

The composition of the instant invention may be added to the paper furnish as hereinbefore described at any convenient point prior to sheet formation. It will be appreciated by those skilled in the art that the exact points of addition are mill specific. Preferably, the composition of this invention is added to thin diluted aqueous cellulosic paper furnish. 50 Any suitable method of addition known in the art can be utilized. A preferred method of addition includes adequate dilution to accomplish dispersion of the composition throughout the furnish.

55 It will be appreciated by those skilled in the art that the process and the composition of the instant invention does not contain a solid or particulate component in comparison to currently available microparticle technology employing such as for example silica, bentonite or alum. The process of this invention, therefore, provides a more economical process of improving drainage, retention, or formation, and combinations thereof, in the pressing and drying of tissue, newsprint, paper or paperboard without insoluble residue or solids buildup.

EXAMPLES

The following examples demonstrate the invention in greater detail. These examples are not intended to limit the scope of the invention in any way. In the examples, the following products were used:

Anionic Polymer A is a 25 weight % active acrylamide sodium acrylate copolymer comprising about 30% by weight sodium acrylate and about 70% by weight acrylamide, available from Calgon Corporation (Pittsburgh, Pennsylvania).

Anionic Polymer B is a 25 weight % active acrylamide copolymer comprising about 5% by weight sodium acrylate and about 95% by weight acrylamide available from Calgon Corporation (Pittsburgh, Pennsylvania).

REAX-905 is a modified sulfonated kraft lignin polymer commercially available from Westvaco, Chemical Division (Charleston Heights, South Carolina) and chemically is a sodium salt of lignosulfonic acid having a weight average molecular weight of about 30,000 and a degree of sulfonation of about 0.8 moles of sulfonic acid groups per 1000 unit weight of the lignin.

Dynasperse A is a modified phenol formaldehyde lignin condensate based on a sulfite lignin having a weight average molecular weight, ranging from about 30,000 to 70,000 commercially available from Ligno-Tech U.S.A., Inc. (Rothschild, Wisconsin)

EXAMPLES 1-4

In Examples 1-4, various formulations were tested for their effectiveness in improving the drainage, retention and formation parameters of a stock aqueous cellulosic furnish of a commercial paper mill. This stock aqueous cellulosic furnish had the following make-up: hardwood/softwood/paper machine broke/recycle, 125 pounds of Ultracote clay (Englehard Corporation, Iselin, New Jersey) per dry ton of finished paper, 30 pounds of alum per dry ton of finished paper, 75 pounds of Ansilex filler (Englehard Corporation, Iselin, New Jersey) per dry ton of finished paper, 112 pounds of Martifil filler (Pleuss-Stauffer International, Stamford, Connecticut) per dry ton of finished paper, and 12 pounds of rosin size per dry ton of finished paper.

TABLE I

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/275 ml)	Formation Index	Retention % Sheet Ash
1.	-	-	-	51	26.5	4.2
2.	B	-	3.0/0	35	20.5	12.8
3.	B	Dynasperse A	1.0/0.5	37	25.4	12.4
4.	B	Dynasperse A	1.0/1.0	36	28.5	12.9

Table I shows the feed rate, drain time, formation index, and % sheet ash (retention) for each example. In these examples and the following examples, the anionic polymer was fed prescreen (at a high rate of shear) followed by the addition of the modified lignin. A high rate of shear, as used herein, is defined as greater than or equal to about 1,000 (rpm). A low rate of shear, as used herein, is defined as less than or equal to about 600 revolutions per minute (rpm). Feed rate is the amount of active polymer added in pounds per ton of solids in the furnish. Table I shows under the column designated "FEED RATE" for Example 2 that 3.0 pounds of active Anionic Polymer B was added per ton of solids in the furnish. Table I shows under the column designated "FEED RATE" for Example 3 that 1.0 pound of active Anionic Polymer B and 0.50 pounds of active modified lignin Dynasperse A were added per ton of solids in the furnish.

Drain time, as used herein, is the time in seconds for a specific amount of water to drain from a testing apparatus, and is a standard technique well known by those skilled in the art. Table I shows under the column designated "DRAIN TIME" that for Example 3, 275 ml of water drained from the treated furnish in 37 seconds. It is desirable to achieve a drainage time in which a specific amount of water is removed from the furnish in the smallest amount of time over the papermaking process.

The formation index was determined by an M/K Formation Tester commercially available by M/K Systems, Inc., Danvers, MA. Percent sheet ash is an indication of filler retention, such as for example, clay, calcium carbonate or titanium dioxide. Percent sheet ash was obtained by ashing preweighed sheet samples at about 900 degrees centigrade employing a standard technique well known by those skilled in the art.

The following two paragraphs set forth the drainage and handsheet test procedures employed in the examples.

Drainage Test Procedure

1. A 500 ml sample of well-mixed aqueous cellulosic paper furnish is added to a one liter beaker.
2. Agitation of the furnish is introduced at 1200 rpm, the anionic polymer is added and the timing sequence is started.
3. At the 30 second mark, the agitation is reduced to 600 rpm.
4. At the 40 second mark, the modified lignin is added depending on the formulation of the example as set forth in Table I through Table VI.
5. At the 60 second mark, the agitation is discontinued and the treated furnish sample is poured into the drainage test apparatus.
6. The test apparatus is then activated and the time required for a specified amount of water to drain from it is measured and recorded.

Handsheet Test Procedure

Steps 1 through 5, above, are duplicated except that the sample size may vary to produce a desired basis weight handsheet, the treated furnish sample is poured into the deckle box of a Noble and Wood handsheet machine and the sheet is prepared employing standard techniques well known by those skilled in the art.

It will be understood that for the Examples herein wherein no anionic polymer was added, the hereinabove Drainage and Handsheet Test Procedures followed the same steps without any polymeric aids being added.

Agitation was provided by a Britt Jar Stirring apparatus fitted with a one inch diameter marine prop.

In Example 1, the furnish was fed to the paper forming apparatus without the addition of an anionic polymer or modified lignin. Table I shows that Example 1 had a drainage time of about 51 seconds per 275 ml of water, a formation index of about 26.5, and a % sheet ash (i.e., retention) of about 4.2.

In Example 2, a feed rate of 3.0 pounds of Anionic Polymer B was added per ton of solids in the furnish. Table I shows that when the composition of Example 2, a commercially available Anionic Polymer B that is currently commercially used for improving the papermaking process, was added to the furnish, a drain time of 35 seconds, a formation index of 20.5, and a % sheet ash (retention) of 12.8 was achieved.

Table I shows that Example 3, containing the composition of the instant invention including Anionic Polymer B and the modified lignin, Dynaspense A, when added to the furnish resulted in a paper product having a drainage time of about 37 seconds, a formation index of about 25.4, and a % sheet ash (retention) of about 12.4. From the data of Table I, it will be appreciated by those skilled in the art that the parameters of drainage and retention are greatly improved when the anionic polymer and modified lignin of the instant invention are added to the furnish in comparison to the results obtained when no additives are added to the furnish. Table I shows that the formation index is relatively unchanged when the composition of the instant invention of Example 3 is added to the furnish when compared to the furnish of Example 1, Table I, having no anionic polymer and modified lignin. It will be appreciated by those skilled in the art that, Table I shows that for Example 2, adding anionic polymer alone to the furnish negatively impacted the formation index while increasing the rate of drainage and % sheet ash retention. It is important to note that, in contrast to the addition of anionic polymer alone shown in Example 2, the composition of the instant invention greatly increased the rate of drainage and % sheet ash retention, and did not generally adversely effect formation, a result not heretofore achieved by those skilled in the art.

Table I shows for Example 4, a composition of the instant invention, a drainage time of 36 seconds per 275 ml, a formation index of 28.5 and a % sheet ash retention of 12.7. The results achieved by employing the composition of the instant invention, set forth in Example 4, clearly shows an improvement in drain time, formation index and % sheet ash retention over Example 1 and Example 2, compositions known in the art. It will be appreciated by those skilled in the art that Table I clearly shows that retention, drainage and formation of the resulting paper are greatly improved when the compositions of the instant invention are employed in the process of the present invention in contrast to the results obtained when employing an anionic polymer alone or when no anionic polymer or modified lignin is added to the stock aqueous cellulosic furnish.

EXAMPLES 5 AND 6

In Examples 5 and 6, a formulation of the present invention was tested for its effectiveness in improving drainage, retention and formation parameters of a stock aqueous cellulosic furnish of a commercial paper mill. This stock aqueous cellulosic furnish had the following make-up: hardwood/softwood/papermachine broke/recycle, 75 pounds of titanium dioxide per dry ton of finished paper, 75 pounds of Ansilex filler per dry ton of finished paper, 160 pounds of Martifil per dry ton of finished paper, and 12 pounds of Neuphor size and alum per dry ton of finished paper. This stock aqueous cellulosic furnish had a pH of about 5.0 and a consistency of 0.8755%. The make-up of the composition of the instant invention of Example 6 is shown in Table II.

TABLE II

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/275 ml)	Formation Index	Retention % Sheet Ash
5.	-	-	-	58	32.4	4.8
6.	B	Dynasperse A	0.50/0.50	53	35.2	11.1

Table II shows that the stock aqueous cellulosic furnish of Example 5 without any additives had a drain time of 58 seconds per 275 ml, a formation index of 32.4 and a % sheet ash retention index of 32.4 and a % sheet ash retention of 4.8. In contrast, when the composition of the instant invention set forth in Example 6 was added to the stock aqueous cellulosic furnish, a drain time of 53 seconds and a % sheet ash retention of 11.1 was achieved. It will be appreciated, therefore, that the composition of Example 6 of the instant invention greatly improved the parameters of drainage, retention and formation of the resulting paper in comparison to the resulting paper when no additives were added to the stock aqueous cellulosic furnish.

Further, the data of Tables I and II clearly show that the compositions of the present invention, Examples 3, 4 and 6, when added to the stock aqueous cellulosic furnish greatly improved the drainage, retention, and formation parameters of the resulting tissue in comparison to currently available additives.

The data of Tables I and II, show that by varying the amounts of the active anionic polymer and active modified lignin components of the compositions of the instant invention, Examples 3, 4 and 6, added per ton of dry weight of solids in the furnish, one or more of the parameters of drainage, retention and formation may be modified as desired.

#### EXAMPLES 7-10

In Examples 7-10 various formulations were tested for their effectiveness in improving the parameters of drainage, retention and formation of tissue made from a neutral stock aqueous cellulosic furnish. This furnish had the following make-up: 50/50 weight % hardwood kraft/softwood kraft, respectively. This neutral stock aqueous cellulosic furnish had a pH of about 6.8, a consistency of about 0.2705% and an ash content of about 23.9%. The make-up of the composition of each Example 7-10 is shown in Table III.

TABLE III

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/150 ml)	Formation Index	Retention % Sheet Ash
7.	-	-	-	51	17.5	1.79
8.	A	-	1.0/0	54	19.9	1.87
9.	A	Dynasperse A	1.0/0.5	38	20.3	1.76
10.	A	Dynasperse A	1.0/1.0	43	20.8	1.97

Table III shows the drainage, formation index and % sheet ash retention results when: (1) no anionic polymer and modified lignin are added to the furnish, Example 7; (2) when Anionic Polymer A is added to the furnish, Example 8; and (3) when the composition of the instant invention, Examples 9 and 10, are added to the furnish. It is clear from the data of Table III that the compositions of the instant invention, Examples 9 and 10, not only greatly improve drainage, further improve the formation index, and generally maintain the parameter of % sheet ash retention. These unexpected improved results relative to drainage, retention, and formation produced by employing the compositions of the instant invention, were heretofore not achieved by others skilled in the art.

#### EXAMPLES 11-27

In Examples 11-27 various formulations were tested for their effectiveness in improving the parameters of drainage, retention and formation for two alkaline stock aqueous cellulosic furnishes and an acid stock aqueous cellulosic furnish. The alkaline stock aqueous cellulosic furnish employed in Examples 11-17 had the following make-up: 10/57/33 weight

EP 0 722 011 A1

% hardwood/softwood/ paper machine broke, respectively, 269 pounds of calcium carbonate per ton of solids in the furnish, 4 pounds of alum per ton of solids in the furnish, and 2.5 pounds of alkyl ketene dimer (AKD) size per ton of solids in the furnish, a consistency of 0.8098%, an ash content of 19.3% and a pH of 7.7. The alkaline stock aqueous cellulosic furnish, used in Examples 23-27, had the following makeup: 70/30 weight % virgin softwood kraft/recycle pulp, respectively, 20 pounds of Cato 15 Starch, an amphoteric wet end starch commercially available from National Starch & Chemical Corp., Bridgewater, New Jersey, per ton of solids in the furnish, 12 pounds of Hi-Phase 35 rosin based size commercially available from Hercules, Inc., Wilmington, Delaware, and 18 pounds of alum per ton of solids in the furnish, a pH of about 7.5, a consistency of about 0.8601% and an ash content of 6.59%. The acid stock aqueous cellulosic furnish used in Examples 18-22 had the same following make-up as the alkaline stock aqueous cellulosic furnish employed in Examples 23-27 with the addition of sufficient alum to achieve a pH of about 5.0, a consistency of about 0.8741% and an ash content of 6.95%. The make-up of the composition of each example is shown in Tables IV, V and VI.

TABLE IV

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/300 ml)	Formation Index	Retention % Sheet Ash
11.	-	-	-	88	42.4	6.1
12.	A	-	0.45/0	66	43.9	11.7
13.	A	Dynasperse A	0.45/0.225	66	50.1	11.6
14.	A	-	0.60/0	59	40.8	11.8
15.	A	Dynasperse A	0.60/0.30	58	49.0	11.8
16.	A	-	0.15/0	87	50.5	10.1
17.	A	Dynasperse A	0.15/0.15	88	51.1	10.9

TABLE V

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/275 ml)	Formation Index	Retention % Sheet Ash
18.	-	-	-	75	39.5	5.6
19.	A	-	0.25/0	61	38.2	6.0
20.	A	Dynasperse A	0.25/0.25	60	38.5	5.9
21.	A	-	0.125/0	67	33.4	5.8
22.	A	Dynasperse A	0.125/0.125	64	37.7	5.9

TABLE VI

Ex.	Anionic Polymer	Modified Lignin	Feed Rate #T/Active	Drain Time (Sec/275 ml)	Formation Index	Retention % Sheet Ash
23.	-	-	-	76	37.7	4.0
24.	A	-	0.370/0	64	39.1	5.7
25.	A	REAX-905	0.375/0	66	41.7	5.8
26.	A	-	0.125/0	70	39.8	5.3
27.	A	REAX-905	0.125/0.125	73	41.5	5.4

Tables IV, V and VI show the drainage retention, and formation results achieved when: (1) no anionic polymer and modified lignin are added to the alkaline stock aqueous cellulosic furnishes, Examples 11 and 23, or acid stock aqueous cellulosic furnish, Example 18; (2) Anionic Polymer A is added to the two alkaline and the one acid stock aqueous cellulosic furnishes, Examples 12, 14, 16, 24 and 26, and Examples 19 and 21, respectively; and (3) the compositions of the instant invention, Examples 13, 15, 17, 25 and 27 and Examples 20 and 22 are added to the two alkaline and one acid stock aqueous cellulosic furnishes, respectively. For example, Example 13, a composition of the instant invention achieved a dramatic increase in drain time (66 seconds/275 ml), formation index (50.1) and % sheet ash retention (11.6) over the alkaline aqueous cellulosic furnish drain time (88 seconds/275 ml), formation index (42.4), and % sheet ash retention (6.1). Further, employing the composition of the instant invention set forth in Example 13, resulted in an improved formation index in comparison to the formation index of 43.9 achieved for Example 12 when adding Anionic Polymer A alone to the alkaline aqueous cellulosic furnish. The drain time and % sheet ash retention remained relatively unchanged when comparing Examples 12 and 13.

Table V shows that the compositions of the instant invention, Examples 20 and 22, when added to the acid aqueous cellulosic furnish improve the drain time while leaving the formation index and % sheet ash retention relatively unchanged.

Table VI shows that the compositions of the instant invention, Examples 25 and 27, when added to the alkaline aqueous cellulosic furnish greatly improved the drain time, formation index and the % sheet ash retention over the results achieved of the aqueous cellulosic furnish having no additives, Example 23, and further improved the parameters of drainage, retention and formation heretofore achieved over the conventional addition of Anionic Polymer A alone, Examples 24 and 26. It is clear from the data of Tables IV, V and VI that the compositions of the instant invention, Examples 13, 15 and 17, Examples 20 and 22, and Examples 25 and 27, respectively, improve drainage, retention or formation, and combinations thereof when added to the alkaline or acid stock aqueous cellulosic furnishes.

From the above data, therefore, it will be appreciated by those skilled in the art that the cellulosic, modified lignin and anionic polymer composition and process for making tissue, newsprint, paper or paperboard of the instant invention significantly improve the parameters of drainage, retention, formation and combinations thereof over conventional known anionic polymer technology and microparticle technology. It will be further understood that employing the compositions of the instant invention enhance the pressing and drying operations of a paper machine.

Whereas particular embodiments of the instant invention have been described for the purposes of illustration, it will be evident to those skilled in the art that numerous variations and details of the instant invention may be made without departing from the instant invention as defined in the appended claims.

## Claims

1. A improved paper furnish composition comprising:
  - (a) an aqueous cellulosic furnish;
  - (b) a high molecular weight anionic polymer; and
  - (c) a modified lignin, wherein the ratio of said anionic polymer : said modified lignin is from about 10:1 to 1:10, on an active basis, wherein said anionic polymer and said modified lignin are each present in an amount of at least about 0.004 per cent by weight, based on dry weight of solids of said aqueous cellulosic furnish, and wherein said improved paper furnish composition exhibits improved drainage, retention and formation, and enhanced pressing and drying with respect to said aqueous cellulosic furnish.
2. The composition of Claim 1 wherein said modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidized lignin, and salts thereof.
3. The composition of Claim 2 wherein said sulfonated lignin has a degree of sulfonation of from about 0.1 to 10 moles of sulfonic acid groups per 1,000 unit weight of said lignin.
4. The composition of claim 2 or claim 3 and wherein said sulfonated lignin has a weight average molecular weight greater than about 2,500.
5. A composition as claimed in any one of claims 1,2,3 or 4 and wherein said anionic polymer is derived from at least one anionic monomer selected from the group consisting of a 2-acrylamido-2-methylpropanesulfonic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, styrene sulfonic acid, vinyl sulfonic acid, vinyl lactic acid, allyl sulfonic acid, alkali metal salts of carboxylic acids, and combinations thereof.
6. The composition of Claim 5 wherein said anionic polymer is a copolymer derived from at least one of said anionic monomers and of at least one of a nonionic monomer selected from the group consisting of acrylamide, methacr-

**EP 0 722 011 A1**

ylamide, diacetone acrylamide, and N,N-dimethyl acrylamide, wherein the weight ratio of said anionic monomer: said nonionic monomer is from about 99:1 to 1:99.

- 5 7. A process in which tissue, newsprint, paper or paperboard is made by forming a furnish composition as claimed in any one of the preceding claims which comprises adding to an aqueous cellulosic furnish at least about 0.004 per cent by weight, based on the dry weight of the solids of said furnish, of (A) a high molecular weight anionic polymer, and at least about 0.004 per cent by weight, based on the dry weight of the solids of said furnish, of (B) a modified lignin, draining said furnish to form a sheet, and drying said sheet, wherein the weight ratio of said anionic polymer (A): said modified lignin (B) is in the range from about 10:1 to 1:10 on an active basis.
- 10 8. The process of claim 7 which includes after draining said furnish to form a sheet, pressing said sheet, and then drying said sheet.
- 15 9. A process in which paper or paperboard is made by forming a furnish composition as claimed in any one of claims 1 to 6 which comprises subjecting an aqueous cellulosic furnish to one or more shear stages, adding to said furnish prior to at least one of said shear stages a high molecular weight anionic polymer, adding to said furnish subsequent to said addition of said anionic polymer and at least one shear stage subsequent thereto, a modified lignin, draining said furnish to form a sheet, and drying said sheet, wherein the weight ratio of said anionic polymer : said modified lignin is in the range from about 10:1 to 1:10, on an active basis, and wherein said anionic polymer and said modified lignin are each present in an amount of at least 0.004 per cent by weight based on the dry weight of solids in said furnish.
- 20 10. Paper or paperboard when made by the process claimed in any one of claims 7 to 9.

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EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 9388

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	US-A-4 347 100 (BRUCATO ALBERT) 31 August 1982 * column 2, line 65 - column 4, line 59 * ---	1,5	D21H23/76 //D21H17:23, 17:42
X	US-A-3 706 629 (MOORE EDGAR E ET AL) 19 December 1972 * the whole document * ---	1,2,5,6	
X	EP-A-0 418 015 (ALBRIGHT & WILSON) 20 March 1991 * claims 1,4,6,7,10,14; examples 1-4,12 * -----	1-8,10	
			<b>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</b>
			D21H
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 11 March 1996	Examiner Nestby, K
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