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(54) **Method of making tissue, newsprint, paper or paperboard**

Verfahren zur Herstellung von Tissuepapier, Zeitungsdruckpapier, Papier oder Karton

Procédé de fabrication de papier tissu, papier journal, papier ou carton

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(56) References cited:
**EP-A- 0 418 015**
**US-A- 3 706 629**
**US-A- 4 347 100**



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## Description

## BACKGROUND OF THE INVENTION

### 1. Field of the invention

**[0001]** This invention relates to the use, by addition to an aqueous cellulosic furnish, of an anionic polymer and a modified lignin in a method for making tissue, newsprint, paper or paperboard giving improved properties in the areas of drainage, retention and formation, which enhance the pressing and drying operations of a paper machine.

### 2. Brief Description of the Background Art

**[0002]** In the production of tissue, newsprint, paper or paperboard from a dilute aqueous cellulosic furnish improvements 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 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 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.

**[0003]** 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 enhance retention is mechanical entrainment.

**[0004]** 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.

**[0005]** 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.

**[0006]** 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 method of the instant invention which results in producing tissue, newsprint, paper or paperboard having improved drainage, retention, and formation properties.

**[0007]** US-A-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 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.

**[0008]** 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.

**[0009]** EP-A-0,418,015 discloses a composition for adding to a paper making stock which includes a lignosulfonate and optionally an anionic charge density extender or modifier comprising an anionic polymer such as an acrylamide. The composition is for active sizing of the paper.

**[0010]** US-A-3 706 629 discloses drainage improvement in paper pulp containing soluble lignin residues by the addition to the pulp of a high molecular weight water-soluble anionic polymeric polyelectrolyte and alum.

## SUMMARY OF THE INVENTION

**[0011]** According to the present invention as described in claim 1 there is provided a method of making paper, paperboard, tissue, newsprint or the like which comprises subjecting an aqueous cellulosic furnish to one or more shear stages, adding to the furnish prior to at least one of the shear stages a first additive comprising a high molecular weight polymer, adding to the furnish subsequent to the addition thereto of the anionic polymer and at least one shear stage subsequent thereof a second additive and draining the furnish to form a sheet wherein the high molecular weight polymer comprises an anionic polymer and wherein the second additive comprises a modified lignin.

**[0012]** The paper etc produced by the method may be further treated by the usual drying and pressing steps following the drainage step.

**[0013]** The method provides improved retention, drainage or formation in the production of the sheets of paper etc, which in turn provides enhanced pressing and drying in the operations of a paper making machine.

**[0014]** In the method of the invention, the weight 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.

**[0015]** In a preferred embodiment of this invention, the modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidised lignin, and salts thereof. In another preferred embodiment of this invention, the sulfonated lignin has a degree of sulfonation of from 0.1 to 10 moles of sulfonic acid groups per 1000 unit weight of the lignin is included.

## DETAILED DESCRIPTION OF THE INVENTION

**[0016]** The instant invention is directed to a method in which sheets of tissue, newsprint, paper, paperboard or the like are made with improved drainage, retention or formation, and combinations thereof which enhances pressing or drying in the manufacture of tissue, newsprint, paper or paperboard, the method being that described earlier in the "Summary of the invention".

**[0017]** 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.

**[0018]** As used herein, the term "active basis" means a concentration of additive based on the solids in the stock solution.

**[0019]** As used herein, the term "paper" includes, but is not limited to, paper, newsprint, tissue, or paperboard.

**[0020]** 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.

**[0021]** 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.

**[0022]** 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).

**[0023]** In a most preferred embodiment of this invention, 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.

**[0024]** In a preferred embodiment of this invention, 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.

**[0025]** Preferably, the weight ratio of the anionic polymer to the modified lignin is from 5:1 to 1:5 and most preferably is from 3:1 to 1:3.

**[0026]** In another embodiment of this invention, the anionic polymer 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.

**[0027]** 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 monomer 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 monomer units may be present.

**[0028]** It will be understood by those skilled in the art that the anionic polymer component and the modified lignin component used in the method of this invention, as described herein, are water soluble or water dispersible.

**[0029]** 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.

**[0030]** An effective amount of the first and second additives in the method of the instant invention should be employed. It will be appreciated by those skilled in the art that the dosage of the additives 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 (0.005 per cent by weight) based on the dry weight of solids in the aqueous cellulosic furnish.

**[0031]** 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.

**[0032]** In a preferred embodiment of this invention the anionic polymer is a copolymer derived from sodium acrylate and acrylamide. Preferably, 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.

**[0033]** The additives employed in 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 additives are 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 additives 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.

**[0034]** It will be appreciated by those skilled in the art that the additives used in the method 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 may include one or more of the following size, calcium carbonate, starch, clay, alum, resin, titanium dioxide and broke.

**[0035]** The anionic polymers used in the method of the invention may be prepared using any conventional polymerization technique that is well known by those skilled in the art.

**[0036]** The additives used in the method of the instant invention may be added to the paper furnish as hereinbefore described at any convenient point (respectively prior to and after a shear stage) 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 additives are added to thin diluted aqueous cellulosic paper furnish. 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 additives throughout the furnish.

**[0037]** It will be appreciated by those skilled in the art that the additives used in the method of the instant invention do not contain a solid or particulate component in comparison to currently available microparticle technology employing such as for example silica, bentonite or alum. The method 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

**[0038]** The following examples are embodiments of the invention which 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:

**[0039]** 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).

**[0040]** 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).

**[0041]** 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.

**[0042]** 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

**[0043]** 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 (6.25% by weight) of Ultracote clay (Englehard Corporation, Iselin, New Jersey) per dry ton of finished paper, 30 pounds (1.5% by weight) 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 (5.6% by weight) of Martifil filler (Pluess-Stauffer International, Stamford, Connecticut) per dry ton of finished paper, and 12 pounds (0.6% by weight) of rosin size per dry ton of finished paper.

**[0044]** In Table I and subsequent Tables H/T active is the active amount in pounds per ton of the anionic polymer and modified lignin components respectively based on the dry weight of the furnish solids. 1 pound per ton is equivalent to 0.05% by weight.

TABLE I

| Ex | Anionic Polymer | Modified Lignin | Feed Rate H/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 |

**[0045]** 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 (0.15% by weight) 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 (0.05% by weight) of active Anionic Polymer B and 0.50 pounds (0.025% by weight) of active modified lignin Dynasperse A were added per ton of solids in the furnish.

**[0046]** 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.

**[0047]** 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 Celsius employing a standard technique well known by those skilled in the art.

**[0048]** The following two paragraphs set forth the drainage and handsheet test procedures employed in the examples.

Drainage Test Procedure

**[0049]**

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

**[0050]** 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.

**[0051]** 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.

**[0052]** Agitation was provided by a Britt Jar Stirring apparatus fitted with a one inch (2.54 cm) diameter marine prop.

**[0053]** 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.

**[0054]** In Example 2, a feed rate of 3.0 pounds (0.15% by weight) 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.

**[0055]** Table I shows that Example 3, embodying the instant invention including use of Anionic Polymer B and the modified lignin, Dynasperse 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.

**[0056]** Table I shows for Example 4, embodying 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 an embodiment 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 embodiment the instant invention is employed 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

**[0057]** In Examples 5 and 6, embodying the present invention a composition 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 (3.75% by weight) of titanium dioxide per dry ton of finished paper, 75 pounds (3.75% by weight) of Ansilex filler per dry ton of finished paper 160 pounds (8% by weight) of Martifil per dry ton of finished paper, and 12 pounds (0.6% by weight) of Neuphor size and alum per dry ton of finished paper. This stock aqueuous 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 H/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 |

**[0058]** 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.

**[0059]** Further, the data of Tables I and II clearly show that the compositions employed in 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.

**[0060]** 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 employed in the method 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

**[0061]** 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 H/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 |

**[0062]** 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 employed in a method embodying the instant invention, Examples 9 and 10, are added to the furnish. It is clear from the data of Table III that the compositions used in 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

**[0063]** 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 % hardwood/softwood/ paper machine broke, respectively, 269 pounds (13.45% by weight) of calcium carbonate per ton of solids in the furnish, 4 pounds (0.8% by weight) of alum per ton of solids in the furnish, and 2.5

pounds (0.125% by weight) 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 (1% by weight) 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 (0.6% by weight) of Hi-Phase 35 rosin based size commercially available from Hercules, Inc., Wilmington, Delaware, and 18 pounds (0.9% by weight) 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 H/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 H/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 H/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 |

**[0064]** 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 used in embodiments 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 used in an embodiment 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 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.

**[0065]** 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.

**[0066]** Table VI shows that the compositions of 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 use of the compositions in embodiments of the instant invention, in 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.

## Claims

1. A method of making paper, paperboard, tissue, newsprint or the like which comprises subjecting an aqueous cellulosic furnish to one or more shear stages, adding to the furnish prior to at least one of the shear stages a first additive comprising a high molecular weight polymer, adding to the furnish subsequent to the addition thereto of the polymer and at least one shear stage subsequent thereof a second additive, draining the furnish to form a sheet, and drying said sheet, wherein the high molecular weight polymer comprises an anionic polymer and wherein the second additive comprises a modified lignin, wherein the weight ratio of the added anionic polymer to the modified lignin is in the range of from 1:10 to 10:1 on an active basis, and wherein the anionic polymer and the modified lignin are each added in an amount of at least 0.005 per cent by weight (0.1 pounds per ton) based on the dry weight of the solids of the furnish.

2. A method according to claim 1 and wherein after draining said furnish to form a sheet, said sheet is pressed, and then dried.

3. A method according to claim 1 or claim 2 and wherein the shear stage following addition of the polymer comprises shearing at a shear speed of at least 1000 revolutions per minute.

4. A method according to any one of the preceding claims and wherein the modified lignin is selected from the group consisting of sulfonated lignin, carboxylated lignin, oxidised lignin, and salts thereof.

5. A method according to claim 4 and wherein the modified lignin is a sulfonated lignin which has a degree of sulfonation of from about 0.1 to 10 moles of sulfonic acid groups per 1,000 unit weight of the lignin.

6. A method according to claim 4 or claim 5 and wherein the modified lignin is a sulfonated lignin which has a weight average molecular weight greater than about 2,500.

7. A method according to any one of the preceding claims and wherein the 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, alkaline metal salts of carboxylic acids, and combinations thereof.

8. A method according to any one of the preceding claims and wherein the anionic polymer is a copolymer derived from at least one anionic monomer and at least one non-ionic monomer, wherein the weight ratio of the anionic monomer: the non-ionic monomer is from about 99:1 to 1:99.

9. A method according to claim 8 and wherein the non-ionic monomer is selected from acrylamide, methacrylamide, diacetone acrylamide and N,N-dimethylacrylamide monomers.

## Patentansprüche

1. Verfahren zur Herstellung von Papier, Pappe, Tuch, Zeitungspapier oder dergleichen, umfassend das Unterwerfen einer wässrigen Cellulose-Beschickung einer oder mehr Scherstufen, Zugeben eines ersten Additivs, welches ein

hochmolekulares Polymer umfasst, zur Beschickung vor zumindest einer der Scherstufen, Zugeben eines zweiten Additivs zur Beschickung nach der Zugabe des Polymers und nach zumindest einer Scherstufe, Entwässern der Beschickung, so dass man eine Bahn erhält, und Trocknen der Bahn, wobei

das hochmolekulare Polymer ein anionisches Polymer umfasst und das zweite Additiv ein modifiziertes Lignin umfasst,
das Gewichtsverhältnis des zugegebenen anionischen Polymers zum modifizierten Lignin auf aktiver Basis von 1:10 bis 10:1 reicht, und
das anionische Polymer und das modifizierte Lignin jeweils in einer Menge von mindestens 0,005 Gew.% (0,1 Pfund pro Tonne), bezogen auf das Trockengewicht der Feststoffe der Beschickung, zugegeben werden.

**2.** Verfahren nach Anspruch 1, wobei dann die Bahn, die beim Entwässern der Beschickung erhalten wird, gepresst und dann getrocknet wird.

**3.** Verfahren nach Anspruch 1 oder 2, wobei nach der Zugabe des Polymers die Scherstufe eine Scherung mit einer Schergeschwindigkeit von mindestens 1000 Umdrehungen pro Minute umfasst.

**4.** Verfahren nach einem der vorhergehenden Ansprüche, wobei das modifizierte Lignin zudem ausgewählt ist aus der Gruppe, bestehend aus sulfoniertem Lignin, carboxyliertem Lignin, oxidiertem Lignin und Salzen davon.

**5.** Verfahren nach Anspruch 4, wobei das modifizierte Lignin zudem ein sulfoniertes Lignin ist, dessen Sulfonierungsgrad von etwa 0,1 bis 10 Mol Sulfonsäuregruppen pro 1000 Gewichtsteile Lignin reicht.

**6.** Verfahren nach Anspruch 4 oder 5, wobei das modifizierte Lignin ein sulfoniertes Lignin mit einem Molekulargewichtsgewichtsmittel größer als etwa 2500 ist.

**7.** Verfahren nach einem der vorhergehenden Ansprüche, wobei sich das anionische Polymer von mindestens einem anionischen Polymer ableitet, ausgewählt aus der Gruppe, bestehend aus 2-Acrylamido-2-methylpropansulfonsäure, Acrylsäure, Methacrylsäure, Maleinsäure, Fumarsäure, Styrolsulfonsäure, Vinylsulfonsäure, Vinylmilchsäure, Allylsulfonsäure, Erdalkalimetallsalzen der Carbonsäuren und Kombinationen davon.

**8.** Verfahren nach einem der vorhergehenden Ansprüche, wobei das anionische Polymer ein Copolymer ist, das aus mindestens einem anionischen Polymer und mindestens einem nichtionischen Monomer abgeleitet ist, wobei das Gewichts-Verhältnis von anionischem Monomer zu nichtionischem Monomer von etwa 99:1 bis 1:99 reicht.

**9.** Verfahren nach Anspruch 8, wobei das nicht-ionische Monomer ausgewählt ist aus Acrylamid-, Methacrylamid-, Diacetonacrylamid- und N,N-Dimethylacrylamid-Monomeren.

**Revendications**

**1.** Procédé de fabrication de papier, de carton, de papier mousseline, de papier journal, ou analogue, qui comprend le fait de soumettre une composition aqueuse cellulosique à une ou plusieurs étapes de cisaillement, d'ajouter à la composition, avant au moins une des étapes de cisaillement, un premier additif comprenant un polymère de masse moléculaire élevée, d'ajouter à la composition, après lui avoir ajouté le polymère et après au moins une étape de cisaillement ultérieure, un deuxième additif, d'égoutter la composition pour former une feuille et de sécher ladite feuille, dans lequel le polymère de masse moléculaire élevée comprend un polymère anionique et dans lequel le deuxième additif comprend une lignine modifiée, le rapport pondéral du polymère anionique ajouté à la lignine modifiée étant dans la gamme de 1:10 à 10:1, sur la base des substances actives, et le polymère anionique et la lignine modifiée étant chacun ajoutés en une quantité d'au moins 0,005 pour cent en poids (0,1 livre par tonne), sur la base du poids sec des matières solides de la composition de fabrication.

**2.** Procédé selon la revendication 1, dans lequel, après l'égouttage de ladite composition pour former une feuille, ladite feuille est pressée, puis séchée.

**3.** Procédé selon la revendication 1 ou la revendication 2, dans lequel l'étape de cisaillement suivant l'addition du polymère comprend un cisaillement à une vitesse de cisaillement d'au moins 1 000 tours par minute.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la lignine modifiée est choisie dans le groupe constitué par la lignine sulfonée, la lignine carboxylée, la lignine oxydée et les sels de ces lignines.

5. Procédé selon la revendication 4, dans lequel la lignine modifiée est une lignine sulfonée possédant un degré de sulfonation d'environ 0,1 à 10 moles de groupes acide sulfonique par 1 000 unités de poids de la lignine.

6. Procédé selon la revendication 4 ou la revendication 5, dans lequel la lignine modifiée est une lignine sulfonée possédant une masse moléculaire moyenne en poids supérieure à environ 2 500.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère anionique est dérivé d'au moins un monomère anionique choisi dans le groupe constitué par l'acide 2-acrylamido-2-méthylpropanesulfonique, l'acide acrylique, l'acide méthacrylique, l'acide maléique, l'acide fumarique, l'acide styrènesulfonique, l'acide vinylsulfonique, l'acide vinyllactique, l'acide allylsulfonique, les sels de métaux alcalins d'acides carboxyliques, el leurs combinaisons.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère anionique est un copolymère dérivé d'au moins un monomère anionique et d'au moins un monomère non ionique, dans lequel le rapport pondéral du monomère anionique au monomère non ionique est d'environ 99:1 à 1:99.

9. Procédé selon la revendication 8, dans lequel le monomère non ionique est choisi parmi les monomères acrylamide, méthacrylamide, diacétone-acrylamide et N,N-diméthylacrylamide.