COMPOSITIONS FOR IMPROVING PHYSICAL STRENGTH PROPERTIES AND HUMIDITY RESISTANCE OF PAPER PRODUCTS

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ABSTRACT

Compositions for enhancing the strength and humidity resistance of lignocellulosic fibrous materials such as paper. The compositions are comprised of at least one lignin derivative and a solvent system whereby the solvent system is comprised of water and at least one organic solvent. Suitable lignin derivatives include but are not limited to lignosulfonate, lignosulfonate/kraft lignin, lignosulfonate/organosolv, and mixtures thereof.

Sugar may be optionally added to further enhance the strength and humidity resistance of lignocellulosic fibrous materials. Suitable sugars include but are not limited to sucrose, fructose, glucose, ribose, mannose maltose, glucose amine, and mixtures thereof. Other optional strength enhancing materials including but not limited to starch, carboxymethyl cellulose, and mixtures thereof may also be added if desired to provide additional strength and humidity resistance.

The strength and humidity resistance of lignocellulosic fibrous materials treated with the compositions of this invention may be further enhanced by the optional application of thermal energy, radiant energy or combinations thereof.

The invention also relates to a method of enhancing the strength and humidity resistance of lignocellulosic fibrous materials.
COMPOSITIONS FOR IMPROVING PHYSICAL STRENGTH PROPERTIES AND HUMIDITY RESISTANCE OF PAPER PRODUCTS

FIELD OF THE INVENTION

[0001] The present invention relates to compositions for improving the physical strength properties and the humidity resistance of materials containing lignocellulosic fibers such as paper and wood products.

BACKGROUND OF THE INVENTION

[0002] It is important that paper products, such as those paper products used for packaging purposes, have the ability to withstand physical forces. Because these materials are exposed to varying environmental conditions, it is also important that these materials have the ability to withstand high humidity conditions (i.e., relative humidity greater than 50%) with limited loss in strength or structural integrity. As paper products are exposed to higher humidity a significant decrease in paper strength is observed.

[0003] It is well known in the art that the strength of paper products can be enhanced by increasing the amount of fiber per unit area of the paper product (i.e., increasing the fiber basis weight). The strength may also be enhanced by the addition of additives such as starch. Humidity resistance of the paper may be enhanced by the addition of additives such as sizing agents.

[0004] The strength and humidity resistance of the paper products may also be enhanced by externally coating the paper with stiffening agents or other hydrophobic materials such as wax. However, in many instances these may not be either economically or environmentally viable options.

[0005] The ability of paper to withstand physical forces can be evaluated by characterizing the strength properties of the paper (for example stiffness, rigidity, burst, tensile strength, compression resistance, tear resistance, etc.). The ability of paper to resist humidity can be evaluated by characterizing paper strength retention at high humidity.

[0006] Lignin is a highly complex polymerized amorphous substance found in lignocellulosic fibrous materials such as wood, grass, and the like. Lignin acts primarily as a glue to bind the fibers together. In the manufacture of paper, lignin is removed from the fibers during the pulping process. This is accomplished either mechanically, chemically, or by a combination of both.

[0007] The chemical pulping process entails cooking lignocellulosic materials with a liquor solution in a heated and pressurized vessel known as a digester. Chemical pulping processes may be differentiated from one another on the basis of the chemicals used to cook the lignocellulosic material.

[0008] One chemical pulping process, known as the sulfite process, utilizes sulfurous acid, and/or its alkali salts to remove the lignin from the lignocellulosic material. The waste liquor arising from the sulfite process, known as spent sulfite liquor contains a lignin derivative known as lignosulfonate. Lignosulfonate in the spent sulfite liquor is generally found in the form of a salt (e.g., sodium, calcium, ammonium, zinc, etc.) of lignosulfonic acid. Lignosulfonate can also be produced by the sulfonation of various lignin derivatives, such as kraft lignin. Though soluble in water at any pH, lignosulfonate is insoluble in most common organic solvents.

[0009] Another chemical pulping process, known as the Kraft process, utilizes sodium hydroxide and sodium sulfide to remove the lignin from the lignocellulosic material. The waste liquor arising from the Kraft process, known as black liquor, contains a lignin derivative known as Kraft lignin. Kraft lignin is soluble in a limited number of organic solvents such as ethylene glycol, diethylene, monoethanolamine, dimethylformamide, and methyl cellosolve. Kraft lignin is also soluble in water at a pH of above 10.5. Additionally, it is soluble in water blended with a limited number of organic solvents (e.g., ethanol/water, acetone/water) wherein the organic solvent constitutes at least about 65% to 90% by weight of the organic solvent/water blend.

[0010] The alcohol pulping process, another type of chemical pulping process, utilizes mixtures of alcohol and water to remove lignin from the wood. The waste liquor arising from the alcohol pulping process contains a lignin derivative known as organosolv. Organosolv lignin is soluble in some organic solvents and in dilute alkali. It is insoluble in water at neutral or acidic pH.

[0011] U.S. Pat. No. 2,703,293 issued to Boehm et al. on Mar. 1, 1955 purports to teach the addition of high molecular weight lignin derivatives to a slurry of lignocellulosic fibers thus improving the resulting paper product. However, such composition adds high levels of lignin and thus may not be suitable for use in the production of dissolving wood or paper products.
wherein the pH of the slurry of lignocellulosic fibers/lignin derivatives is adjusted to a pH range of 2 to 7 to effect precipitation of the lignin derivatives. At least 35% by weight of the lignin derivatives must have a molecular weight over 5000.

[0017] In light of the prior art, it is unexpected to find that mixtures of kraft lignin with lignosulfonate having a weight ratio of as much as 5:1 kraft lignin to lignosulfonate are soluble at a pH of about 6 to 8 in blends of water and organic solvent(s) wherein the water constitutes as much as about 80% by weight of the water/organic solvent blend.

[0018] Conversely, it is unexpected to find that lignosulfonate is soluble in blends of organic solvent(s) and water wherein the organic solvent constitutes as much as about 80% by weight of the water/organic solvent blend.

[0019] Additionally, it is surprising to find that paper samples treated with the compositions of the present invention exhibit significant increases in strength versus untreated paper without requiring additional processing steps or the addition of more fiber or other strength enhancing additives.

[0020] Furthermore, it is surprising to find that paper samples treated with the compositions of the present invention exhibit a higher retention of strength at higher humidity versus untreated paper.

[0021] The benefit of adding the compositions of the present invention to paper is the ability of the compositions to provide enhanced strength to the paper without requiring the addition of more fiber per unit area (i.e.; increased basis weight) versus untreated paper.

[0022] Another benefit of adding the compositions of the present invention to paper is the improved adherence of the compositions to the paper fibers versus the prior art.

[0023] A further benefit of adding the compositions of the present invention to paper is the ability of the compositions to provide a heavier weight paper product without requiring the addition of more fiber to achieve the additional weight.

[0024] Yet a further benefit of the compositions of the present invention is the ability of the compositions to provide paper with improved retention of strength at higher humidity versus untreated paper.

[0025] Yet another further benefit of the compositions of the present invention is the ability to adjust the strength and humidity resistance characteristics of the paper by varying the ratio of the lignin derivatives used.

SUMMARY OF THE INVENTION

[0026] This invention pertains to a composition for enhancing the strength and humidity resistance of a lignocellulosic fibrous material. The active composition comprises from about 1% to 80% total active solids by weight and from about 20% to 99% of a solvent system by weight.

[0027] As used herein “total active solids” refers to solids contained in the compositions of the present invention which contribute to enhancing the strength or humidity resistance of the lignocellulosic fibrous material. As used herein “inert solids” refers to solids contained in the compositions of the present invention which do not contribute to enhancing the strength or humidity resistance of the lignocellulosic fibrous material. As used herein “active composition” refers to the solvent system and the total active solids contained in the composition.

[0028] The solids are comprised of a lignin derivative selected from the group consisting of lignosulfonate, lignosulfonate/kraft lignin, lignosulfonate/organosolv, and mixtures thereof. The solvent system comprises water and at least one organic solvent.

[0029] The organic solvent which comprises from about 5% to 80% of the solvent system by weight is selected from the group consisting of alcohol, ketone, aldehyde, ether, and mixtures thereof.

[0030] Optionally, the composition may also include active solids such as sugar wherein the ratio of lignin derivative to the added sugar is from about 5:1 to 1:5 based on the weight of the total active solids in the composition. The sugar is selected from the group consisting of ribose, mannose, maltose, fructose, glucose, glycogen amine, sucrose, and mixtures thereof.

[0031] The composition may also optionally include other active solids (i.e.; additives) such as but not limited to: starch, carboxymethyl cellulose, sodium silicate, xylan, acrylic polymers, vinyl polymers and mixtures thereof. The ratio of lignin derivative to optional additives is from about 5:1 to 1:5 based on the weight of the total active solids in the composition.

[0032] In one embodiment the active composition comprises from about 1% to 80% lignosulfonate solids by weight and from about 20% to 99% of a solvent system by weight. The solvent system comprises water and at least one organic solvent. The organic solvent may be acetone, ethanol, or mixtures thereof. The organic solvent comprises from about 5% to 80% of the solvent system by weight.

[0033] In another embodiment the active composition comprises from about 1% to 80% total active solids by weight wherein the total active solids are comprised of lignosulfonate and kraft lignin. The ratio of lignosulfonate to kraft lignin is from about 5:1 to 1:5 based on the weight of the total active solids. The active composition also comprises from about 20% to 99% of a solvent system by weight wherein the solvent system is comprised of water and at least one organic solvent. The organic solvent may be acetone, ethanol, or mixtures thereof. The organic solvent comprises from about 5% to 80% of the solvent system by weight.

[0034] The invention also includes a method of enhancing the strength and humidity resistance of a paper product by:

[0035] a) providing a lignocellulosic fibrous material;

[0036] b) providing an active composition comprised of:

[0037] i) from about 1% to 80% total active solids by weight wherein the total active solids are comprised of a lignin derivative selected from the group consisting of lignosulfonate, lignosulfonate/kraft lignin, lignosulfonate/organosolv, and mixtures thereof;

[0038] ii) from about 20% to 99% of a solvent system by weight wherein the solvent system comprises water and at least one organic solvent;
c) applying the composition to the lignocellulosic fibrous material at an addition rate of about 1% to 80% total active solids based on the weight of dry fiber in the lignocellulosic fibrous material;

d) optionally applying thermal energy, radiant energy, or combinations thereof to the lignocellulosic fibrous material.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to compositions added to lignocellulosic fibrous materials used in the manufacture of paper and wood products which enhance the physical strength and humidity resistance of the products. As used herein “compositions” refers to finely dispersed or solubilized solids in solvent systems comprised of water and organic solvents. Lignocellulosic fibrous materials such as those containing cellulosic fiber or combinations of cellulosic and noncellulosic fiber may be effectively treated with the compositions of this invention.

Though the compositions of this invention may be used to enhance the strength and humidity resistance of any type of lignocellulosic fibrous material, they are especially useful for enhancing the strength and humidity resistance of paper products such as corrugated containers, cartonboard, boxboard, linerboard, corrugating medium, paper plates, and other similar paper products.

The compositions of this invention are comprised of lignin derivatives and a solvent system containing water and at least one organic solvent. Sugars may be optionally added to the compositions. A non-exclusive list of other strength enhancing additives which may be optionally added to the compositions of the present invention include but are not limited to starch, carboxymethyl cellulose, and hemi-cellulose.

The strength and humidity resistance of the paper products may be further enhanced by optionally applying thermal energy, radiant energy, or combinations thereof to the lignocellulosic fibrous materials treated with the compositions of this invention. Examples of thermal or radiant energy which may be applied to the treated paper include but are not limited to oven baking, high frequency heating, electron beam curing, photon curing (for example ultraviolet light, x-ray, and gamma ray), and combinations thereof.

The Compositions

Referring to the compositions of the present invention in more detail, the compositions comprise a lignin derivative(s) dissolved or finely dispersed in a solvent system. The solvent system comprises water and at least one organic solvent. Optionally sugar(s) and/or other strength enhancing additives may be added to the compositions of the present invention. Though the pH of the compositions of the present invention can range between about 2 to 11; it is unexpected to find that blends of kraft lignin with lignosulfonate having a weight ratio of as much as 5:1 kraft lignin to lignosulfonate are soluble at a pH of about 6 to 8 in blends of water and organic solvent(s) wherein the water constitutes as much as about 80% by weight of the solvent system.

The compositions of the present invention are comprised of about 1% to 80% total active solids by weight, preferably about 10% to 60% total active solids by weight, and more preferably about 20% to 50% total active solids by weight. The active solids are comprised of one or more lignin derivatives. The active solids may also optionally include at least one sugar and/or one or more other optional additives described below.

Lignin Derivative(s):

The compositions of the present invention include one or more lignin derivatives. As used herein, “lignin derivatives” refers to lignin based materials which are byproducts of the wood pulping process.

Suitable lignin derivatives include but are not limited to lignosulfonate, kraft lignin, organosolv lignin, and mixtures thereof.

While not wishing to be bound by theory, it is believed that compositions containing blends of lignosulfonate and kraft lignin; lignosulfonate, kraft lignin and organosolv; or lignosulfonate and organosolv further enhance the humidity resistance of the paper as compared to compositions which contain lignosulfonate alone. This appears to be especially beneficial to the retention of paper strength at relative humidity above 50%. Proprietary, organosolv may be substituted wholly or in part for kraft lignin.

Lignosulfonates useful in the compositions of this invention include but are not limited to salts of lignosulfonic acid. Non-limiting examples of salts of lignosulfonic acid include sodium lignosulfonate, ammonium lignosulfonate, magnesium lignosulfonate, zinc lignosulfonate, and preferably calcium lignosulfonate.

A suitable lignosulfonate for this purpose is a spent sulfite liquor solution containing about 40% total active solids (i.e.; total active solids consist of calcium lignosulfonate), 10% inert solids, and 50% water commercially sold as LIGNOSITE 50 available from Georgia-Pacific Corporation of Atlanta, Ga.

A suitable kraft lignin useful in the compositions of this invention is INDIULIN AF, containing about 97% total active solids (i.e.; total active solids consist of kraft lignin) and 3% inert solids, sold by Westvaco Corporation of New York, N.Y.

A suitable organosolv lignin useful in the compositions of the present invention is ALCELL, sold by Tembec Inc. of Montreal, Canada.

Solvent System:

The compositions of the present invention include a solvent system comprised of water and one or more organic solvent(s). The main function of the solvent system is to solubilize or finely disperse the lignin derivatives and any optional sugars present.

The solvent system comprises from about 20% to 99% by weight of the active composition, preferably from about 40% to 90% by weight of the active composition, and more preferably from about 50% to 80% by weight of the active composition. Solvent systems which may be used in the present invention include mixtures of water and organic solvents. Suitable organic solvents include alcohol (e.g.; methanol, propanol, butanol, and preferably ethanol), ketone (e.g.; methyl ethyl ketone, diacetone alcohol and preferably...
acetone), aldehyde (e.g., acetaldehyde, propionaldehyde, and furfural), and ether (e.g., ethyl propyl ether, dioxane, and methyl cellosolve). The organic solvent comprises from about 5% to 80% of the solvent system by weight, preferably from about 10% to 60% of the solvent system by weight, and more preferably from about 40% to 60% of the solvent system by weight.

[0059] Optional Sugar(s):

[0060] Sugars may be optionally added to the compositions of this invention. Not wishing to be bound by theory, lignin derivatives and sugars in blends of water and organic solvent(s) are thought to more easily penetrate fiber structures in comparison to lignin derivatives alone in blends of water and organic solvent(s). The ratio of lignin derivative to the optional sugar added to the composition is from about 5:1 to 1:5 based on the weight of total active solids, preferably from about 4:1 to 1:4 based on the weight of total active solids, and more preferably from about 3:1 to 1:3 based on the weight of the total active solids.

[0061] When sugar is added in conjunction with mixtures of lignosulfonate and kraft lignin or lignosulfonate and organosolv lignin, the ratio of lignosulfonate-to-kraft lignin (or organosolv lignin)-to-sugar is from about 5:1:3 to 3:1:5 based on the weight of total active solids, preferably from about 4:1:2 to 2:1:4 based on the weight of total active solids, and more preferably from about 3:1:1 to 1:1:3 based on the weight of total active solids.

[0062] Sugars useful in the present invention include but are not limited to ribose, mannose, maltose, preferably fructose, glucose, and glucose amine, more preferably sucrose, and mixtures thereof.

[0063] Other Optional Additives:

[0064] Other optional additives including but not limited to starch, carboxymethyl cellulose, sodium silicate, xylan, acrylic polymers, vinyl polymers, and mixtures thereof, may also be added to the compositions of this invention if desired in order to provide additional strength and humidity resistance. The ratio of lignin derivative to optional additive(s) is from about 5:1 to 1:5 based on the weight of total active solids, preferably from about 4:1 to 1:4 based on the weight of total active solids, and more preferably from about 3:1 to 1:3 based on the weight of the total active solids.

[0065] Application

[0066] Addition rates of the compositions to the lignocellulosic fibrous material range from about 1% to 80% total active solids based on the weight of dry fiber in the lignocellulosic fibrous material, preferably from about 5% to 60% total active solids based on the weight of dry fiber in the lignocellulosic fibrous material, and more preferably from about 10% to 50% total active solids based on the weight of dry fiber in the lignocellulosic fibrous material.

[0067] The compositions may be added to the lignocellulosic fibrous material at any point prior to use by the consumer including but not limited to during the paper manufacturing process or preferably after the paper manufacturing process (e.g. during the converting operation, etc.). Though the compositions may be added to the lignocellulosic fibrous material irrespective of the lignocellulosic fibrous material moisture content, typically, the compositions are added to lignocellulosic fibrous materials having a consistency of at least about 0.005%, preferably of at least about 0.05%, more preferably of at least about 0.30%, more preferably of at least about 0.75%, and even more preferably of at least about 0.90%.

[0068] The lignocellulosic fibrous material may be treated with one or more of the compositions. If more than one composition is used, the lignocellulosic fibrous material may be treated sequentially or simultaneously with more than one composition. For example, the felt side of a paper product may be treated with a composition. Simultaneously or sequentially, the wire side of the paper product may be treated with the same composition or a composition different from that used to treat the felt side. Another example includes treating the same side of the paper sequentially or simultaneously with two or more different compositions.

[0069] Methods for Applying the Compositions to Lignocellulosic Fibrous Materials

[0070] There are many methods familiar to those of ordinary skill in the art for applying the compositions to lignocellulosic fibrous materials such as paper products. Different methods may be used to simultaneously or sequentially apply the compositions. Examples of these methods include but are not limited to coating (for example roll coating, blade coating, and air knife application), spraying, dipping, printing, and impregnation. Suitable methods of applying the compositions of the present invention to lignocellulosic fibrous materials are disclosed in U.S. Pat. No. 3,647,525 issued to Dahlgren on Mar. 7, 1972, U.S. Pat. No. 4,558,616 issued to Menner on May 13, 1986, U.S. Pat. No. 4,702,943 issued to Long on Oct. 27, 1987, U.S. Pat. No. 4,915,989 issued to Menner et al. on Apr. 10, 1990, U.S. Pat. No. 4,982,686 issued to Long on Jan. 8, 1991, and EP 816,562 published Jan. 7, 1998, the disclosures of which are incorporated herein by reference.

[0071] After application to the lignocellulosic fibrous material, the compositions are allowed to dry. Any drying means familiar to those skilled in the art may be used for this purpose.

[0072] Optional Application of Thermal or Radiant Energy

[0073] Thermal or radiant energy may be optionally applied to lignocellulosic fibrous materials such as paper products treated with the compositions of this invention. Thermal or radiant energy may be utilized to further enhance the strength and humidity resistance of the treated paper. Examples of thermal or radiant energy which may be used include but are not limited to oven baking, high frequency heating, electron beam curing, photon curing (for example ultraviolet light, x-ray, and gamma ray), microwave, and combinations thereof. Preferred temperatures for thermal energy applications vary from about 50° C. to 300° C., preferably from about 60° C. to 270° C., and most preferably from about 80° C. to 250° C.

[0074] Preferred Embodiments

[0075] While particular embodiments of the present invention are illustrated and described below, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.
In one embodiment of the present invention, the composition comprises finely dispersed or solubilized lignosulfonate solids and a solvent system comprised of water and at least one organic solvent. The lignosulfonate solids comprise from about 1% to 80% of the active composition by weight, preferably from about 10% to 60% of the active composition by weight, and more preferably from about 20% to 50% of the active composition by weight.

The solvent system comprises from about 20% to 99% of the active composition by weight, preferably from about 40% to 90% of the active composition by weight, and more preferably from about 50% to 80% of the active composition by weight.

The organic solvent comprises from about 5% to 80% of the solvent system by weight, preferably from about 10% to 70% of the solvent system by weight, and more preferably from about 40% to 60% of the solvent system by weight.

Optionally, sugar may be added to the lignosulfonate such that the total active solids comprise from about 1% to 80% by weight of the active composition, preferably from about 10% to 60% by weight of the active composition, and more preferably from about 20% to 50% by weight of the active composition. The ratio of lignosulfonate to sugar is from about 5:1 to 1:5 based on the weight of total active solids, preferably from about 4:1 to 1:4 based on the weight of total active solids, and more preferably from about 3:1 to 1:3 based on the weight of the total active solids.

In another embodiment of the present invention, the composition comprises finely dispersed or solubilized lignosulfonate and Kraft lignin solids and a solvent system comprised of water and at least one organic solvent. The lignosulfonate and Kraft lignin solids comprise from about 1% to 80% by weight of the active composition, preferably from about 10% to 60% by weight of the active composition, and more preferably from about 20% to 50% by weight of the active composition.

The ratio of lignosulfonate to Kraft lignin is from about 5:1 to 1:5 based on the weight of total active solids, preferably from about 4:1 to 1:4 based on the weight of total active solids, and more preferably from about 3:1 to 1:3 based on the weight of total active solids.

The solvent system comprises from about 20% to 99% of the active composition by weight, preferably from about 40% to 90% of the active composition by weight, and more preferably from about 50% to 80% of the active composition by weight.

The organic solvent comprises from about 5% to 80% of the solvent system by weight, preferably from about 10% to 70% of the solvent system by weight, and more preferably from about 40% to 60% of the solvent system by weight.

Optionally, sugar may be added to the lignosulfonate and Kraft lignin such that the total active solids comprise from about 1% to 80% by weight of the active composition, preferably from about 10% to 60% by weight of the active composition, and more preferably from about 20% to 50% by weight of the active composition. The ratio of lignosulfonate-to-Kraft lignin-to-sugar is from about 5:1:3 to 3:1:5 based on the weight of total active solids, preferably from about 4:1:2 to 2:1:4 based on the weight of total active solids, and more preferably from about 3:1:1 to 1:1:3 based on the weight of total active solids.

This embodiment provides the ability to adjust the strength and humidity resistance of the paper by varying the ratio of lignosulfonate to Kraft lignin in the composition. For example, lignosulfonate is less costly per pound than Kraft lignin. However, as lignosulfonate tends to be more water soluble than Kraft lignin, it does not adhere to the fibers as readily as Kraft lignin at high humidity. Hence, in a situation where paper strength and economics are more crucial than humidity resistance, it may be desirable to utilize a higher proportion of lignosulfonate. Conversely, in a situation where humidity resistance is crucial, it may be desirable to increase the proportion of Kraft lignin.

**EXAMPLES**

**Paper Sample Preparation For Examples 1-7**

The paper samples utilized for testing in Examples 1-7 were single-wall C-flute corrugated board comprised of a top liner, bottom liner, and C-flute medium having a total grammage of about 485 g/m² or a heavier weight single-wall C-flute corrugated board having a total grammage of about 770 g/m². The samples were all cut to a dimension of 2 inches in length by 2 inches in width. The samples were then weighed. Some of the samples having a grammage of 485 g/m² were treated with the compositions described in Examples 1-5 below by dipping in the composition for 1 minute. Some of these treated samples were further subjected to thermal treatment by heating for 15 minutes at 200° C.

**All samples** (both treated and untreated) were then preconditioned for 24 hours at 145°F and approximately 5% to 10% relative humidity. After preconditioning, the samples were divided up and conditioned for 24 hours and 73°F at either 50% RH or 95% RH. After conditioning, the samples were weighed and edgewise compressive strength tests ("ECT") run in accordance with Tappi Standard T 811 om-95. The results of these tests are reported in Table 1.

**Example 1**

A composition was formulated by blending 93 g of acetone and 15 g of water with 250 g of LIGNOSITE 50 (i.e., LIGNOSITE 50 contains 40% calcium lignosulfonate solids, 10% inert solids, and 50% water), to form an active composition comprised of about 70% solvent system and 30% calcium lignosulfonate solids by weight of the active composition. The solvent system in the composition was comprised of about 60% water and 40% acetone by weight of the solvent system. The pH of the composition was approximately 7.

**Example 2**

For comparison purposes, a prior art composition was formulated by blending 108 g of water with 250 g of LIGNOSITE 50 to form an active composition comprised of
about 70% solvent system and 30% calcium lignosulfonate solids by weight of the active composition. The solvent system in the composition was comprised of 100% water by weight of the solvent system. The pH of the composition was approximately 7.

Example 3

[0093] A composition was formulated by blending 93 g of ethanol and 15 g of water with 250 g of LIGNOSITE 50 to form an active composition comprised of about 70% solvent system and 30% calcium lignosulfonate solids by weight of the active composition. The solvent system in the composition was comprised of 60% water and 40% ethanol by weight of the solvent system. The pH of the composition was approximately 7.

Example 4

[0094] A composition was formulated by blending 73 g of acetone with 250 g of LIGNOSITE 50 and 50 g of sucrose. Water in the amount of 15 g was evaporated from this blend, to form an active composition comprised of about 55% solvent system and 45% total active solids by weight of the active composition. The solvent system in the composition was comprised of 60% water and 40% acetone by weight of the solvent system. The total active solids were comprised of 67% calcium lignosulfonate solids and 33% sucrose solids by weight of the total active solids. The pH of the composition was approximately 7.

Example 5

[0095] A composition was formulated by blending 200 g of acetone and 50 g of water with 71 g of INDULIN AT (i.e.; INDULIN AT contains 97% kraft lignin solids and 3% inert solids) and 250 g of LIGNOSITE 50 to form an active composition comprised of about 69% solvent system and 31% total active solids by weight of the active composition. The solvent system in the composition was comprised of 47% water and 53% acetone by weight of the solvent system. The total active solids were comprised of 41% kraft lignin solids and 59% calcium lignosulfonate solids by weight of the total active solids. The pH of the composition was approximately 7.

Example 6

[0096] A composition was formulated by blending 174 g of acetone and 32 g of INDULIN AT with 300 g of LIGNOSITE 50 to form an active composition comprised of about 68% solvent system and 32% total active solids by weight of the active composition. The solvent system in the composition was comprised of 46% water and 54% acetone by weight of the solvent system. The total active solids were comprised of 79% calcium lignosulfonate solids and 21% kraft lignin solids by weight of the total active solids. The pH of the composition was approximately 7.

Example 7

[0097] A composition was formulated by blending 200 g of acetone and 106 g of water with 35 g of INDULIN AT. This was then mixed with 250 g of LIGNOSITE 50 and 40 g of sucrose to form an active composition comprised of about 71% solvent system and 29% total active solids by weight of the active composition. The solvent system in the composition was comprised of 54% water and 46% acetone by weight of the solvent system. The total active solids were comprised of 57% calcium lignosulfonate solids, 20% kraft lignin solids, and 23% sucrose solids by weight of the total active solids. The pH of the composition was approximately 7.

[0098] Referring to Table I, for each condition tested, the data reported is based on an average of four samples. Column 1 identifies the type paper sample tested. Column 2 indicates the average approximate grammage of the paper sample before treatment. Column 3 indicates which composition (if any) was added to the sample. Column 4 indicates the average approximate grammage of the paper sample after treatment. Column 5 indicates if the sample was heated prior to preconditioning.

[0099] Column 6 indicates the average percentage weight gain (i.e.; add-on) after conditioning for 24 hours at 73° F. and 50% RH for those samples found in Table I, rows 2-13 versus the untreated control sample found in Table I, row 1.

[0100] Column 7 indicates the average ECT for those samples tested after conditioning for 24 hours at 73° F. and 50% RH. Column 8 indicates the % change in average ECT after conditioning for 24 hours at 73° F. and 50% RH for the samples found in rows 2-13 versus the untreated control sample found in row 1.

[0101] Column 9 indicates the average ECT for those samples tested after conditioning for 24 hours at 73° F. and 95% RH. Column 10 indicates the % change in average ECT after conditioning for 24 hours at 73° F. and 95% RH for the samples found in rows 2-13 versus the untreated control sample found in row 1.

EXAMPLE 8

[0102] The paper samples utilized for testing in Example 8 were either linerboard having a grammage of about 172 g/m² (i.e.; ULTRASTAK PLUS 70, available from Georgia-Pacific Corporation of Atlanta, Ga.) or a heavier weight linerboard having a grammage of about 270 g/m² (i.e.; ULTRASTAK PLUS 120). Some of the lighter weight samples (i.e.; samples having a grammage of 172 g/m²) were treated by saturating the felt side of the samples with the composition of Example 5. A pilot scale MIPLY pressure saturator available from Vits-Maschinenbau GmbH of Langenfeld, Germany was used for this purpose.

[0103] All of the samples (both treated and untreated) were cut to a dimension of 6 inches in length by 0.5 inches in width and then weighed. The samples were preconditioned for 24 hours at 145° F. and approximately 5% to 10% relative humidity. After preconditioning, the samples were divided up and conditioned for 24 hours and 73° F. at either 50% RH or 80% RH. After conditioning, the samples were weighed again and ring crush testing (RCT) performed in accordance with Tappi Standard T 818 cm-97. The results of the tests are shown in Table II.

[0104] Referring to Table II, for each condition tested, the data reported is based on an average of eight samples. Column 1 identifies the type paper sample tested. Column 2 indicates the average approximate grammage of the paper sample before treatment. Column 3 indicates which composition (if any) was added to the sample. Column 4 indicates the average approximate grammage after treat-
ment. Column 5 indicates the average percentage weight gain after conditioning for 24 hours at 73°F and 50% RH for the samples found in rows 2 and 3 versus the untreated control sample found in row 1.

[0105] Column 6 indicates the average cross direction (“CD”) RCT for the samples tested after conditioning for 24 hours at 73°F and 50% RH. Column 7 indicates the % change in average CD RCT after conditioning for 24 hours at 73°F and 50% RH for the samples found in rows 2 and 3 versus the untreated control sample.

[0106] Column 8 indicates the average machine direction (“MD”) RCT for the samples conditioned at 50% RH. Column 9 indicates the % change in average MD RCT after conditioning at 50% RH versus the untreated control sample.

[0107] Column 10 indicates the average CD RCT for the samples tested after conditioning for 24 hours at 73°F and 80% RH. Column 11 indicates the % change in average CD RCT after conditioning at 80% RH versus the untreated control sample. Column 12 indicates the average MD RCT for the samples after conditioning at 80% RH. Column 13 indicates the % change in average MD RCT after conditioning at 80% RH versus the untreated control sample.

**TABLE I**

<table>
<thead>
<tr>
<th>Paper Sample Description</th>
<th>2 Avg. Approx. Grammage Before Treatment (g/m²)</th>
<th>3 Composition Added (Example No.)</th>
<th>4 Avg. Approx. Grammage After Treatment (g/m²)</th>
<th>5 Heated at 200°F C. for 15 Min.</th>
<th>6 Avg. Approx. Weight % Add-on at 50% RH vs. Untreated Control</th>
<th>7 Avg. MD ECT at 50% RH</th>
<th>8 % Change in Avg. ECT at 50% RH vs. Untreated Control</th>
<th>9 Avg. MD ECT at 95% RH</th>
<th>10 % Change in Avg. MD ECT at 95% RH vs. Untreated Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>None (Untreated Control)</td>
<td>—</td>
<td>No</td>
<td>25 ± 3.7</td>
<td>—</td>
<td>10 ± 2.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>770</td>
<td>—</td>
<td>No</td>
<td>—</td>
<td>59%</td>
<td>56 ± 0.8</td>
<td>125%</td>
<td>22 ± 2.0</td>
<td>122%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 1</td>
<td>766</td>
<td>No</td>
<td>58%</td>
<td>77 ± 4.6</td>
<td>210%</td>
<td>9.8 ± 1.7</td>
<td>-3%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 1</td>
<td>727</td>
<td>Yes</td>
<td>50%</td>
<td>83 ± 4.7</td>
<td>232%</td>
<td>15.3 ± 0.3</td>
<td>51%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 2</td>
<td>626</td>
<td>No</td>
<td>29%</td>
<td>53 ± 3.9</td>
<td>114%</td>
<td>11.4 ± 2.5</td>
<td>13%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 2</td>
<td>599</td>
<td>Yes</td>
<td>24%</td>
<td>60 ± 6.3</td>
<td>139%</td>
<td>14.8 ± 0.9</td>
<td>47%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 3</td>
<td>685</td>
<td>Yes</td>
<td>41%</td>
<td>83 ± 6.0</td>
<td>231%</td>
<td>17.3 ± 1.0</td>
<td>71%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 4</td>
<td>823</td>
<td>Yes</td>
<td>70%</td>
<td>102 ± 2.7</td>
<td>308%</td>
<td>16.4 ± 1.0</td>
<td>62%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 5</td>
<td>668</td>
<td>No</td>
<td>38%</td>
<td>75 ± 4.3</td>
<td>202%</td>
<td>22 ± 1.2</td>
<td>12%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 5</td>
<td>669</td>
<td>Yes</td>
<td>38%</td>
<td>84 ± 2.8</td>
<td>238%</td>
<td>34 ± 1.6</td>
<td>239%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>483</td>
<td>Example 6</td>
<td>721</td>
<td>No</td>
<td>40%</td>
<td>58 ± 4.2</td>
<td>134%</td>
<td>17 ± 0.5</td>
<td>77%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>483</td>
<td>Example 6</td>
<td>649</td>
<td>Yes</td>
<td>34%</td>
<td>71 ± 5.8</td>
<td>185%</td>
<td>22 ± 2.7</td>
<td>126%</td>
</tr>
<tr>
<td>Single Wall “C” Flute</td>
<td>485</td>
<td>Example 7</td>
<td>650</td>
<td>Yes</td>
<td>34%</td>
<td>75 ± 4.4</td>
<td>200%</td>
<td>28 ± 2.0</td>
<td>180%</td>
</tr>
</tbody>
</table>

**TABLE II**

| Paper Sample Description | 2 Avg. Approx. Grammage (g/m²) | 3 Composition Added (Example No.) | 4 Avg. Approx. Grammage (g/m²) | 5 Weight % Add-on at 50% RH vs. Untreated Control | 6 Avg. MD ECT at 50% RH (bf/6 in.) | 7 % Change in Avg. MD ECT at 50% RH vs. Untreated Control | 8 Avg. MD ECT at 95% RH (bf/6 in.) | 9 % Change in Avg. MD ECT at 95% RH vs. Untreated Control | 10 Avg. CD RCT at 80% RH (bf/6 in.) | 11 % Change in Avg. CD RCT at 80% RH vs. Untreated Control | 12 Avg. MD RCT at 95% RH vs. Untreated Control |
|--------------------------|---------------------------------|-----------------------------------|-----------------------------------|---------------------------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-------------------------------|
| Linerboard               | 172 (Untreated Control)        | —                                 | 52 ± 4                           | 73 ± 7                          | 41 ± 2                        | 59 ± 5                          | —                             | —                               | —                               | —                               | —                               | —                               |

[0108]
What is claimed is:

1. A composition for enhancing the strength and humidity resistance of a lignocellulosic fibrous material, said composition comprising:
   a) from about 1% to 80% total active solids by weight of the active composition wherein said solids are comprised of a lignin derivative, said lignin derivative selected from the group consisting of lignosulfonate, lignosulfonate/kraft lignin, lignosulfonate/organosolv, and mixtures thereof;
   b) a solvent system comprising from about 20% to 99% by weight of the active composition, said solvent system comprising water and at least one organic solvent.

2. The composition of claim 1 wherein said organic solvent is selected from the group consisting of alcohol, ketone, aldehyde, ether, and mixtures thereof.

3. The composition of claim 2 wherein said organic solvent is selected from the group consisting of ethanol, acetone, and mixtures thereof.

4. The composition of claim 3 wherein said organic solvent comprises from about 5% to 80% by weight of the solvent system.

5. The composition of claim 1 wherein said total active solids further comprise at least one sugar, the ratio of said lignin derivative to said sugar is from about 5:1 to 1:5 based on the weight of said total active solids.

6. The composition of claim 5 wherein said sugar is selected from the group consisting of ribose, mannose, maltose, fructose, glucose, glucose amine, sucrose, and mixtures thereof.

7. The composition of claim 6 wherein said sugar is sucrose.

8. The composition of claim 1 wherein said total active solids further comprise an additive selected from the group consisting of starch, carboxymethyl cellulose, sodium silicate, xylan, acrylic polymers, vinyl polymers, and mixtures thereof, the ratio of said lignin derivative to said additive is from about 5:1 to 1:5 based on the weight of said total active solids.

9. The composition of claim 1 wherein said lignosulfonate is selected from the group consisting of calcium lignosulfonate, sodium lignosulfonate, ammonium lignosulfonate, magnesium lignosulfonate, zinc lignosulfonate, and mixtures thereof.

10. The composition of claim 9 wherein said lignosulfonate is calcium lignosulfonate.

11. The composition of claim 1 wherein said organic solvent comprises from about 5% to 80% by weight of said solvent system.

12. The composition of claim 11 wherein said organic solvent comprises from about 10% to 70% by weight of said solvent system.

13. A composition for enhancing the strength and humidity resistance of a lignocellulosic fibrous material, said composition comprising:
   a) from about 1% to 80% total active solids by weight of the active composition wherein said total active solids are comprised of lignosulfonate;
   b) a solvent system comprising from about 20% to 99% by weight of said active composition, said solvent system comprising water and at least one organic solvent wherein said organic solvent is selected from the group consisting of acetone, ethanol, or mixtures thereof, said organic solvent comprising from about 5% to 80% of said solvent system by weight.

14. The composition of claim 13 wherein said total active solids further comprise sugar, the ratio of said lignosulfonate to said sugar is from about 5:1 to 1:5 based on the weight of said total active solids.

15. A composition for enhancing the strength and humidity resistance of a lignocellulosic fibrous material, said composition comprising:
   a) from about 1% to 80% total active solids by weight of the active composition wherein said total active solids are comprised of lignosulfonate and kraft lignin, the ratio of said lignosulfonate to said kraft lignin is from about 5:1 to 1:5 based on the weight of said total active solids;
   b) a solvent system comprising from about 20% to 99% by weight of said active composition, said solvent system comprising water and at least one organic solvent wherein said organic solvent is selected from the group consisting of acetone, ethanol, or mixtures thereof, said organic solvent comprising from about 5% to 80% of said solvent system by weight.

16. The composition of claim 15 wherein said total active solids further comprise sugar, the ratio of said lignosulfonate to said kraft lignin to said sugar is from about 5:1:3 to about 3:1:5 based on the weight of said total active solids.

| Paper Sample Description | MD RCT at 80% RCT at 50% Unshrunk | MD RCT at 80% RCT at 50% RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control | MD RCT at 80% RCT at 50% Control |
|--------------------------|------------------------------------|-------------------------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| 1 Liner board | 270 None | 57% 87 ± 4 | 67% | 111 ± 10 | 52% 56 ± 6 | 37% 89 ± 7 | 51% |
| 2 Liner board | 270 Example 5 | 210 22% | 60% | 104 ± 14 | 42% 62 ± 11 | 51% 90 ± 4 | 53% |

TABLE II-continued
17. A method of enhancing the strength and humidity resistance of a paper product said method comprising the steps of:
a) providing a lignocellulosic fibrous material;
b) providing a composition comprised of:
i) from about 1% to 80% total active solids by weight of the active composition wherein said solids are comprised of a lignin derivative said lignin derivative selected from the group consisting of lignosulfonate, lignosulfonate/kraft lignin, lignosulfonate/organosolv, and mixtures thereof;
ii) a solvent system comprising from about 20% to 99% by weight of said active composition said solvent system comprising water and at least one organic solvent;
c) applying said composition to said lignocellulosic fibrous material wherein the addition rate of said composition to said lignocellulosic fibrous material is from about 1% to 80% total active solids based on the weight of dry fiber in said lignocellulosic fibrous material.

18. The method of claim 17 further comprising applying thermal energy, radiant energy, or combinations thereof to said lignocellulosic fibrous material.

19. The method of claim 17 wherein said total active solids further comprise at least one sugar whereby the ratio of said lignin derivative to said sugar is from about 5:1 to 1:5 based on the weight of said total active solids.