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(54) **PAPER MAKING PROCESS AND STARCH COMPOSITIONS COMPRISING A CROSSLINKING AGENT FOR USE IN SAME**

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(57) **ABSTRACT**

The present invention relates to methods for manufacturing paper or paperboard with improved strength and drainage by introduction into the fiber furnish, prior to sheet formation, an aqueous starch dispersion of a gelatinized, self-retaining starch, and an aldehyde generating compound or a glyoxal releasing compound. The present invention further relates to pre-gelatinized starch compositions comprising an aqueous mixture of a pre-gelatinized starch and an aldehyde generating compound or a glyoxal releasing compound.

PAPER MAKING PROCESS AND STARCH COMPOSITIONS COMPRISING A CROSSLINKING AGENT FOR USE IN SAME

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention provides methods of manufacturing paper and paperboard materials having increased strength, and more particularly provides a method of making paper and paperboard materials possessing increased wet and dry strength. The present invention further provides starch compositions suitable for use in the methods of making paper or paperboard materials with increased strength provided by the invention. The compositions comprise at least one type of gelatinized starch and at least one aldehyde generating compound, or more preferably a glyoxal releasing compound, which typically is activated during the drying process of the paper making process.

[0003] 2. Background

[0004] Industrial starch may be utilized in a wide variety of paper making applications, such as a coating binder or surface treatment for paper and paperboard materials, and as a strength and retention wet end additive in papermaking. Starch compositions are frequently prepared as an aqueous dispersion which is capable of being added to the pulp slurry. For many commercial applications starch is gelatinized prior to addition of the starch to the pulp slurry, and may be carried out by the starch provider or the paper manufacturer. Gelatinization typically occurs after starch granules are dispersed as a slurry in water and the resultant aqueous slurry is heated to a temperature of 50° C. or more, and more typically to a temperature of 95° C. or more. In certain gelatinization methods, the starch granules are heated to a temperature of more than 100° C., such as starch gelatinized using a commercial jet cooker or another pressurized steam cooker. Under such conditions starch grains tend to absorb water, swell and eventually rupture to allow starch fragments and molecules to disperse in the water. This process of rupturing and dispersion is generally referred to as "gelatinization" and is an irreversible reaction, resulting in a relatively thick starch dispersion.

[0005] The crosslinking of starch with multi-functional reagents, which are reactive with starch hydroxyl groups, is well known. Glyoxal and polyaldehyde compounds and resins have been previously utilized as crosslinkers. Simple mixing of glyoxal with a starch dispersion rapidly affords a gel. However, glyoxal is infinitely soluble in water and does not interact efficiently with other chemicals or compositions, particularly heterogeneous materials dispersed in small quantities in large volumes of water, e.g., such as gelatinized starch molecules or cellulosic fibers present in the wet-end of the paper making process. Thus, addition of glyoxal or other low molecular weight crosslinkers directly to the wet-end of the papermaking process has not been found to provide benefit to end product of the paper making process.

[0006] U.S. Pat. No. 6,303,000 issued to Floyd et al. (Floyd '000) discloses gelatinized starch compositions crosslinked with a glyoxal resin and the use of same in paper making. The crosslinked starch composition of Floyd '000 comprise the reaction product formed by heating starch with a blocked glyoxal resin such as those resins recited in U.S. Pat. No. 4,695,606 (Floyd, '606) during the gelatinization process. The heating process forms a gelatinized starch that is crosslinked by the glyoxal resin. More particularly, Floyd '000 discloses the addition of a crosslinked gelatinized starch composition to the wet end of the paper making process. In other words, prior to addition to the wet end, the starch is heated with the blocked glyoxal resin to gelatinize the starch and induce a crosslinking reaction between the glyoxal and the starch. The Floyd '000 patent further discloses that the glyoxal resin can be pre-mixed with the starch prior to the gelatinization heating step or added during the starch gelatinization process. Floyd suggests that pre-mixing the starch and blocked glyoxal resin prior to the gelation process or addition of the blocked glyoxal resin during the gelatinization process, affords superior material having improved shelf stability.

[0007] The Floyd '606 patent describes paper binder compositions comprising a mixture of an acrylic or vinyl polymer with a blocked glyoxal resins, e.g., such as the reaction product of glyoxal and a urea or a cyclic urea. More particularly, the blocked glyoxal resin is a condensation polymer of glyoxal blocked with urea, cyclic ureas such as ethylene urea, 4,5-dihydroxyethylene urea and propylene urea, carbamates, glycols, or polyols.

[0008] In Floyd '000 the addition levels of the gelatinized starch composition demonstrated to affect a significant improvement in paper or paperboard strength are relatively high at the level of 40 lb or more dry starch composition per ton of dry pulp. It is well known in the art of papermaking that significant issues may occur when relatively high levels of starch are used to produce paper, including high cost, high levels of effluent Biological Oxygen Demand (BOD), reduction in paper opacity, machine deposits, and problems with dewatering and drying the paper or paperboard leading to reduced production rates. It would thus be desirable to have paper strength compositions that are effective at lower levels of usage.

[0009] As an alternative approach, it would be desirable to have a starch composition including a stabilized aldehyde generating compound or a stabilized glyoxal compound that is activated upon drying of the formed paper and paperboard materials. It would also be desirable to provide methods of making paper and paperboard with increased strength using such starch compositions.

SUMMARY OF THE INVENTION

[0010] The present invention provides storage stabile, pre-gelatinized starch compositions that include at least one glyoxal releasing compound or at least one aldehyde generating compound. These compounds facilitate a process of manufacturing paper or paperboard having improved strength using less pre-gelatinized starch composition than previous paper or paperboard manufacturing processes. Preferably, the manufacturing processes of certain embodiments of the invention provide paper or paperboard materials with equivalent strength and a reduced basis weight when compared to paper or paperboard materials made with previous paper manufacturing processes.

[0011] In accord with the present invention, a method for manufacturing paper and paperboard materials with increased strength, the method comprising the steps of:

[0012] providing a storage stabile, gelatinized starch composition comprising gelatinized starch and at least one aldehyde generating compound capable of forming at least two or more covalent bonds to functional groups present in the starch or fiber when the aldehyde generating compound is heated above an activation temperature;

[0013] providing a fiber slurry suitable for use in making paper or paperboard;

[0014] incorporating a gelatinized starch composition into the fiber slurry;

[0015] forming a paper or paperboard sheet; and

[0016] heating the paper or paperboard sheet at a temperature above the activation temperature of the aldehyde generating compound and which is sufficient to dry the paper or paperboard sheet.

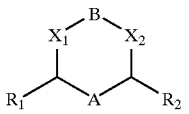
[0017] The present invention also provides gelatinized starch compositions which are suitable for strengthening paper prepared by the methods of the invention where the starch composition comprises a mixture of:

[0018] a self-retaining gelatinized starch;

[0019] at least one aldehyde blocking compound capable of blocking aldehyde residues; and

[0020] an aldehyde generating compound according to the Formula I:

I



[0021] wherein

[0022] A is an optionally substituted methylene group, an optionally substituted α,ω-C_{2-4}-alkylene, or a single bond;

[0023] B is carbonyl, thiocarbonyl, or an optionally substituted 1,2-ethylene residue;

[0024] X_1 and X_2 are independently selected from the group consisting of oxygen and NR_3;

[0025] R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, optionally substituted C_{1-20}alkyl, optionally substituted C_{1-20}alkoxy, optionally substituted urea, optionally substituted thiourea, or R_1 and R_2, taken in combination, form a N,N'-divalent urea;

[0026] R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, optionally substituted C_{1-20}alkyl, a blocked dialdehyde compound (e.g., a stabilized dialdehyde compound) comprising at least two protected aldehyde residues, and a blocked glyoxal residue, where the blocked glyoxal residue is a 1-hydroxy-2-(protected aldehyde residue)-ethan-1-yl group;

[0027] wherein the aldehyde generating compound according to Formula I thermally degrades to generate at least one equivalent of glyoxal or a compound comprising two or more aldehyde residues when heated above an activation temperature; and

[0028] wherein the aldehyde blocking compound loading is at least 10 molar % of the aldehyde generating compound.

[0029] Preferred aldehyde generating compounds according to Formula I include glyoxal releasing compounds such as those compounds in which (i) A is a single bond and R_1 and R_2 are hydroxyl, or (ii) R_3 contains a glyoxal residue that can generate glyoxal, or compounds satisfying both conditions (i) and (ii).

[0030] Other aspects of the invention are discussed infra.

[0031] For purposes of the present invention, the term "self-retaining starch" means any starch, that through its functionality, has the property of being retained effectively in the paper or paperboard web during the process of sheet consolidation during the papermaking process. Though not limited to the general description, this usually requires that the starch have a net cationic charge for retention on the generally anionic fibers used to make paper and paperboard.

[0032] Thus, a "self-retaining gelatinized starch" is added to the papermaking slurry at some point before consolidation of the paper web and is substantially retained or adsorbed onto the fiber components of the slurry and becomes a component of the paper or paperboard.

[0033] For the purposes of the present invention, the term "aldehyde generating compound" refers to materials that upon activation by heat will generate compounds containing two or more reactive aldehyde residues that are then available for reaction With functional groups that generally react in an aqueous environment with aldehyde groups. Moreover, the term aldehyde generating compound includes those compounds capable of generating polyaldehyde compounds upon thermal degradation and compounds capable of generating one or more aldehyde groups in sequence such that two or more covalently connected aldehyde residues are generated during the thermal degradation of the aldehyde generating compound. Particularly preferred aldehyde generating compounds release glyoxal or generate one or two aldehyde groups which are derived from glyoxal.

[0034] For the purposes of the present invention, the term "glyoxal releasing compound" refers to materials that upon activation by heat will generate compounds containing reactive glyoxal moieties that are then available for reaction with functional groups that generally react in an aqueous environment with glyoxal. In general, glyoxal releasing compounds are a subset of aldehyde generating compounds.

[0035] For the purposes of the present invention, the term "blocked aldehyde residue" refers to structures in which at least one aldehyde group is hindered from forming free or active aldehyde groups under storage or wet end paper making conditions. Similarly, the term "blocked glyoxal residue," as used herein, refers to structures in which the glyoxal releasing group is hindered from forming a free or active aldehyde group under the current conditions present.

[0036] For the purposes of the present invention, the term "stabilizing agent" refers to any compound or combination of compounds capable of forming a cyclic ring structure which comprises one or more equivalents of glyoxal as a part of the ring structure or as a substituent thereof. Preferred stabilizing agents are capable of masking, blocking or otherwise protecting one, or preferably, two aldehyde functional groups of glyoxal from undergoing undesired reactions prior to the drying step of the paper making process.

[0037] For the purposes of the present invention, the term "aldehyde blocking agent" refers to any compound or combination of compounds capable of masking, blocking or otherwise protecting an aldehyde functional group and preferably are capable of masking or blocking aldehyde functional groups in an aqueous environment. Typically preferred aldehyde blocking agents release or unmask the aldehyde group at elevated temperatures such as the temperature used to dry paper or paperboard.

DETAILED DESCRIPTION OF THE INVENTION

[0038] Self-retaining gelatinized starch compositions of the present invention comprise an aqueous dispersion containing at least one self-retaining gelatinized starch and at least one aldehyde generating compound or glyoxal releasing compound that are suitable for imparting increased strength to paper. Preferred aqueous self-retaining gelatinized starch compositions of the invention comprise at least one glyoxal releasing compound comprising at least one blocked glyoxal residue which is capable of generating reactive aldehyde groups and/or releasing glyoxal upon heating the glyoxal releasing compound. Typically preferred aqueous self-retaining gelatinized starch compositions of the invention are resistant to gelation and viscosity increase during storage, particularly when stored at a temperature of 40° C. or less. Moreover, preferred gelatinized starch compositions of the invention have a sufficiently low viscosity to permit the composition to flow.

[0039] The self-retaining gelatinized starch compositions of the present invention are particularly useful for manufacturing paper or paperboard sheet having increased strength at the same basis weight, or having the same strength with reduced basis weight. The methods for manufacturing paper or paperboard typically comprise providing a fiber slurry suitable for use in making paper; incorporating a gelatinized starch composition into the fiber slurry; forming the paper and paperboard materials; heating the paper and paperboard materials at a temperature above the activation temperature of the aldehyde generating compound or glyoxal releasing compound and which is sufficient to dry the paper.

[0040] Starch sources useful in the practice of the present invention include, for example, potato, corn, waxy corn, red milo, white milo, wheat, tapioca, and the like. Preferred starch sources include potato, corn and wheat. Preferably, the starch composition comprises a self retaining starch, i.e. a starch having a net cationic charge. In particular starches containing cationic or a combination of cationic and anionic functional groups, the so-called amphoteric starches, including all the known commercial cationic and amphoteric starches, can be used. More preferably, the starch composition, which comprises a commercial pregelatinized cationic starch such as, but not limited to, those sold by Penford, Grain Processing Corporation (GPC), National Starch, Raisio and Staley, are suitable for use in the compositions and paper making methods provided by the invention.

[0041] In addition to the pre-gelatinized starches, any of the mill cooked starches commonly used in the wet-end of the paper machine can be used if cooled prior to addition of the glyoxal releasing compound.

[0042] Gelatinized starch composition suitable for use in the paper making methods of the invention generally comprise between about 0.5% to about 50% of at least one aldehyde generating compound or glyoxal releasing compound based on the combined dry weight of the starch and aldehyde generating compound or glyoxal releasing compound. Preferred gelatinized starch compositions comprise between about 0.5% and about 10, or 15, or 20, or 25, or 30% by dry weight of at least one aldehyde generating compound or glyoxal releasing compound.

[0043] The gelatinized starch compositions of this invention can be used alone or in combination with other separately added strength developing additives commonly used in papermaking. These include cationic guar gum, cationic hemicelluloses, chitosan, anionic polyacrylamide strength resins as described in U.S. Pat. No. 5,543,446, cationic reactive polyacrylamide strength resins as described in U.S. Pat. No. 3,556,932, and the various types of commercial wet strength resins including the common and well known aminopolyamide-epichlorohydrin and melamine- or urea-formaldehyde resins. They also can be used in combination with the separately added starch added to the wet end or as a surface treatment, as is commonly practiced in the papermaking process to develop strength or improve other aspects of papermaking.

[0044] In particularly preferred methods of the invention, the aldehyde generating compound thermally degrades at the temperature sufficient to dry paper thereby releasing or generating enough aldehyde groups to crosslink the starch and/or fiber. Preferred aldehyde generating compounds generate one or more equivalents of glyoxal and/or glyoxal equivalents during the thermal degradation. More preferably, at least a portion of the released glyoxal from the thermal degradation of the aldehyde generating compound reacts with functional groups present in the starch or on the fiber surface to form covalent crosslinks between two starch molecules or particles or between starch and fiber.

[0045] In preferred methods of making paper provided by the invention, the aldehyde generating compound is a glyoxal releasing compound which comprises a reaction product of at least one molar equivalent of glyoxal with between about 0.25 and about 5 molar equivalents of one or more stabilizing agents. More preferably, the glyoxal releasing compound comprises the reaction product of between one and three equivalents of glyoxal and between one and two, three or four equivalents of one or more stabilizing agents.

[0046] Typically preferred stabilizing agents suitable for use in the glyoxal releasing compounds or aldehyde generating compounds of the invention include those chemical compounds capable of reacting with at least one and preferably at least two aldehyde groups to form one or two thermally labile functional groups which release an unblocked aldehyde functional group when heated above an

activation temperature. In preferred embodiments, the activation temperature is between about 75° C. and about 250° C., more preferably the activation temperature is between about 90° C. and about 150° C.

[0047] In preferred methods of making paper, the gelatinized starch composition may comprise a glyoxal releasing compound prepared by the reaction of

[0048] at least one molar equivalent of glyoxal; and

[0049] between about 0.5 and about 3 molar equivalents of stabilizing agents selected from the group consisting of optionally substituted urea, optionally substituted thiourea, optionally substituted imidazolidin-2-one, and optionally substituted tetrahydropyrimidin-2-one.

[0050] In certain preferred methods of making paper provided by the present invention, the gelatinized starch composition further comprises one or more aldehyde blocking compounds which are capable of reversibly blocking residual aldehyde residues present in the gelatinized starch composition, e.g., unblocked aldehyde groups in the aldehyde generating compound, the glyoxal releasing compound or aldehyde groups present in glyoxal containing byproducts which may be generated during the synthesis of the glyoxal releasing compound. In preferred embodiments, aldehyde blocking compounds can be selected from amines, particularly alkyl amines, alcohols such as alkanols, alkylene glycols and other aldehyde blocking compounds, which liberate a free aldehyde upon exposure to elevated temperatures. Certain preferred aldehyde blocking compounds include, for example, methanol, ethanol, 1- and 2-propanol, propylene glycol, and the like.

[0051] In preferred papermaking methods of the invention, the gelatinized starch composition may further comprise one or more optionally substituted C_{1-20}alcohol, optionally substituted C_{2-20}alkylene glycol or a combinations thereof may be also incorporated, as an aldehyde blocking compound to block residual aldehydes present in the aldehyde generating compound, the glyoxal releasing compound or aldehyde groups present in byproducts produced during the preparation of the glyoxal releasing compound.

[0052] More preferably, paper making methods of the invention comprise the use of a glyoxal releasing compound which is the reaction product of

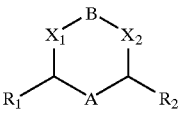
[0053] between 0.5 and 2 molar equivalent of glyoxal; and

[0054] between about 1 and about 3 molar equivalent of stabilizing agents selected from the group consisting of urea, thiourea, 4,5-dihydroxy-imidazolidin-2-one, and 4-hydroxy-5-(C_{1-10}-alkyl)-tetrahydro-pyrimidin-2-one.

[0055] Particularly preferred gelatinized starch compositions which are suitable for use in the paper making processes of the invention include compositions in which the glyoxal releasing compound is the reaction product of glyoxal and at least one stabilizing agent selected from urea, thiourea, 4,5-dihydroxy-imidazolidin-2-one, and 4-hydroxy-5-(C_{1-10}-alkyl)-tetrahydro-pyrimidin-2-one and further comprise at least 10 molar percent of an aldehyde blocking compound selected from propylene glycol, methanol, ethanol, n-propanol, and isopropanol.

[0056] In other preferred methods of making paper, the aldehyde generating compound is a compound according to Formula I:

I



[0057] wherein

[0058] A is an optionally substituted methylene group, an optionally substituted α,ω-C_{2-4}alkylene, or a single bond;

[0059] B is carbonyl, thiocarbonyl, or an optionally substituted 1,2-ethylene residue;

[0060] X_1 and X_2 are independently selected from the group consisting of oxygen and NR_3;

[0061] R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, optionally substituted C_{1-20}alkyl, optionally substituted C_{1-20}alkoxy, optionally substituted urea, optionally substituted thiourea, or

[0062] R_1 and R_2, taken in combination, form a N,N'-divalent urea;

[0063] R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, optionally substituted C_{1-20}alkyl, and blocked glyoxal residues, where the blocked glyoxal residue is a 1-hydroxy-2-(protected aldehyde residue)-ethan-1-yl group;

[0064] wherein the aldehyde generating compound according to Formula I thermally degrades to generate at least one equivalent of a poly(aldehyde) compound when heated above an activation temperature; and

[0065] wherein the aldehyde blocking compound loading is at least 10 molar % of the aldehyde generating compound.

[0066] Preferred aldehyde generating compounds of Formula (I) are glyoxal releasing compounds. More preferred glyoxal releasing compounds according to Formula I include those compounds wherein (i) A is a single bond and R_1 and R_2 are hydroxyl, or (ii) R_3 contains a glyoxal residue that can generate glyoxal, or compounds satisfying both conditions (i) and (ii).

[0067] Preferred glyoxal releasing compounds according to Formula I which are suitable for use in the paper making methods of the invention include those compounds in which:

[0068] R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, methanol, ethanol, urea, or

[0069] R_1 and R_2, taken in combination, form a N,N'-divalent urea;

[0070] R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, methyl, and ethyl, or

[0071] R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

[0072] Other preferred glyoxal releasing compounds according to Formula I which are suitable for use in the paper making methods of the invention include those compounds in which:

[0073] X_1 and X_2 are NR_3;

[0074] A is a single bond;

[0075] B is a carbonyl or thiocarbonyl group; and

[0076] R_1 and R_2 are independently selected from hydroxyl, C_{1-6}alkoxy, or blocked glyoxal residues.

[0077] Still other preferred glyoxal releasing compounds according to Formula I which are suitable for use in the paper making methods of the invention include those compounds in which:

[0078] X_1 and X_2 are NR_3;

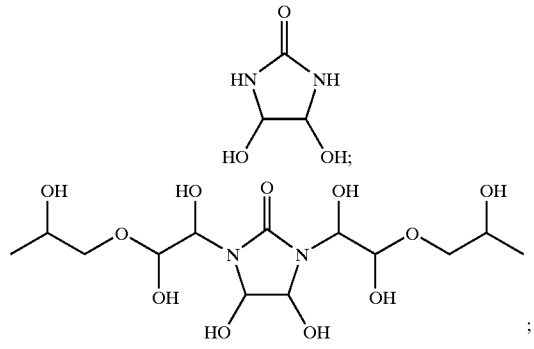
[0079] A is a 1,1-C_{1-6}alkylene group;

[0080] B is a carbonyl or thiocarbonyl group;

[0081] R_1 and R_2 are independently selected from hydrogen, hydroxyl, C_{1-6}alkoxy, or blocked glyoxal residues; and

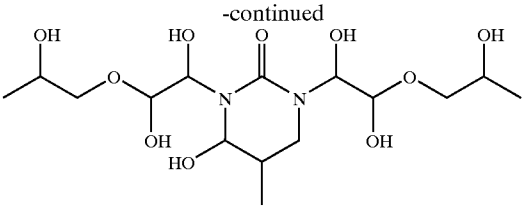
[0082] R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_4-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

[0083] Particularly preferred aldehyde generating compound or glyoxal releasing compounds suitable for use in the paper making processes of the invention include, but are not limited to, the following compounds:



; and

-continued



[0084] Each of which may optionally be mixed with one or more aldehyde blocking compounds such as from propylene glycol, methanol, ethanol, n-propanol, and isopropanol. More preferably the glyoxal releasing compounds are admixed with at least 10, 15, 20, 25, or more molar percent of an aldehyde blocking compound. While not wishing to be bound by theory, addition of the aldehyde blocking compound generally prevents the aldehyde generating compound or glyoxal releasing compound from comprising unblocked aldehyde residues and thereby increases the stability of gelatinized starch compositions comprising one or more aldehyde generating compound or glyoxal releasing compound provided by the invention.

[0085] Other preferred methods of the invention include those in which the starch component of the starch composition further comprises a cationic starch which is functionalized with at least one ammonium salt. More preferably, the ammonium salts incorporated into the starch composition comprises an alkylated ammonium cation and a small counter anion. Particularly preferred ammonium salts include tetraalkylammonium halide salts, N-alkyl pyridinium halide salts, or salts generated from the use of Dow Quat™ 180, a common cationizing agent for preparing cationic starch.

[0086] Preferred starch compositions of the invention comprise a self retaining starch, i.e. a starch having a net cationic charge. In particular, commercial pregelatinized cationic starch such as, but not limited to, those sold by Penford, Grain Processin Corporation (GPC), National Starch, Raisio and Staley are suitable for use in the gelatinized starch compositions provided by the invention. Starch sources such as potato, corn, waxy corn, red milo, white milo, wheat, tapioca, and the like may be used. Preferred starch sources include potato, corn and wheat.

[0087] In addition to the pre-gelatinized starches any of the mill cooked starches commonly used in the wet-end of the paper machine may be used if cooled prior to addition of the aldehyde generating compound or glyoxal releasing compound.

[0088] Gelatinized starch compositions of the invention typically comprise between about 0.5% to about 50% of at least one aldehyde generating compound or glyoxal releasing compound based on the combined dry weight of the starch and aldehyde generating compound or glyoxal releasing compound.

[0089] The gelatinized starch compositions of the invention comprise the use of an aldehyde generating compound or a glyoxal releasing compound which is stable in the presence of starch at about room temperature. That is, gelatinized starch compositions of the invention comprise an aldehyde generating compound or a glyoxal releasing com-

pound which does not substantially react with starch at room temperature, that is the reaction with starch is sufficiently sluggish as to preclude the accumulation of significant amounts of the reaction product during routine storage time periods.

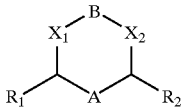
[0090] In particularly preferred gelatinized starch compositions of the invention, the aldehyde generating compound or glyoxal releasing compound thermally degrades at the temperature sufficient to dry paper or paperboard thereby releasing one or more equivalents of glyoxal or reactive aldehyde groups. More preferably, at least a portion of the aldehyde groups released from the thermal degradation of the aldehyde generating compound or glyoxal releasing compound reacts with functional groups of the starch or fiber to form covalent crosslinks between two starch moieties or between a starch moiety and a fiber.

[0091] In preferred gelatinized starch compositions of the invention, composition comprises:

[0092] a self-retaining gelatinized starch;

[0093] at least one aldehyde blocking compound capable of blocking aldehyde residues of glyoxal; and

[0094] an aldehyde generating compound according to the Formula I:



I

[0095] wherein

[0096] A is an optionally substituted methylene group, an optionally substituted C_{2-4}alkylene group, or a single bond;

[0097] B is carbonyl, thiocarbonyl, or an optionally substituted 1,2-ethylene residue;

[0098] X_1 and X_2 are independently selected from the group consisting of oxygen and NR_3;

[0099] R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, optionally substituted C_{1-20}alkyl, optionally substituted C_{1-20}alkoxy, optionally substituted urea, optionally substituted thiourea, or

[0100] R_1 and R_2, taken in combination, form a N,N'-divalent urea;

[0101] R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, optionally substituted C_{1-20}alkyl, and blocked glyoxal residues, where the blocked glyoxal residue is a 1-hydroxy-2-(protected aldehyde residue)-ethan-1-yl group;

[0102] wherein the aldehyde generating compound according to Formula I thermally degrades to generate at least one equivalent of glyoxal when heated above an activation temperature; and

[0103] wherein the aldehyde blocking compound loading is at least 10 molar % of the glyoxal releasing compound.

[0104] Preferred aldehyde generating compounds of Formula (1) are glyoxal releasing compounds. More preferred glyoxal releasing compounds according to Formula I include those compounds wherein (i) A is a single bond and R_1 and R_2 are hydroxyl, or (ii) R_3 contains a glyoxal residue that can generate glyoxal, or compounds satisfying both conditions (i) and (ii).

[0105] Particularly preferred gelatinized starch compositions of the invention include those compositions which are a homogeneous solution or a dispersion in an aqueous media.

[0106] Other preferred gelatinized starch composition comprise an aldehyde generating compound or a glyoxal releasing compound according to Formula I wherein the aldehyde generating compound or glyoxal releasing compound reacts with starch or gelatinized starch with a rate sufficiently slow to permit storage of the composition for at least one day at room temperature. More preferably, the gelatinized starch composition is stable for at least three days or for at least seven days. Particularly preferred gelatinized starch compositions are stable for two weeks or more or for a month or more.

[0107] Other preferred gelatinized starch composition of the invention include those compositions in which the aldehyde blocking compound is selected from the group consisting of C_{1-20}alcohols, C_{2-20}alkylene glycols, and C_{1-20}alkylamines. More preferably the aldehyde blocking compound is selected from the group consisting of methanol, ethanol, propanol (n-propanol, isopropanol, or a mixture thereof), ethylene glycol, and propylene glycol.

[0108] Yet other preferred gelatinized starch composition of the invention include glyoxal releasing compounds according to Formula I wherein

[0109] R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, methanol, ethanol, urea, or

[0110] R_1 and R_2, taken in combination, form a N,N'-divalent urea;

[0111] R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, methyl, and ethyl, or

[0112] R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

[0113] Additional preferred gelatinized starch composition of the invention include glyoxal releasing compounds according to Formula I wherein

[0114] X_1 and X_2 are NR_3;

[0115] A is a single bond;

[0116] B is a carbonyl or thiocarbonyl group; and

[0117] R_1 and R_2 are independently selected from hydroxyl, C_{1-6}alkoxy, or blocked glyoxal residues.

[0118] Still other preferred gelatinized starch composition of the invention include glyoxal releasing compounds according to Formula I wherein

[0119] X_1 and X_2 are NR_3;

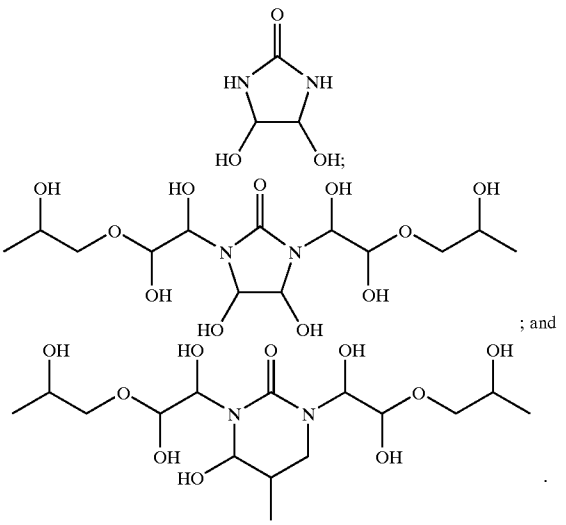
[0120] A is a 1,1-C_{1-6}alkylene group;

[0121] B is a carbonyl or thiocarbonyl group;

[0122] R_1 and R_2 are independently selected from hydrogen, hydroxyl, C_{1-6}-alkoxy, or blocked glyoxal residues; and

[0123] R_3 is a stabilized glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

[0124] Particularly preferred gelatinized starch composition of the invention include aldehyde generating compounds or glyoxal releasing compounds according to Formula I, wherein the aldehyde generating compound or glyoxal releasing compound comprises at least one compound selected from the group consisting of compounds of the formulae:



[0125] An aqueous self-retaining gelatinized starch composition comprises a starch which is self-retaining due to a net cationic charge. The net charge of the starch also assists the gelatinized starch in absorbing and retaining the aldehyde generating compounds or glyoxal releasing compound from the aqueous media of the composition. The net charge of the starch may also increase the strength of the interaction between the starch and aldehyde generating compounds or glyoxal releasing compound and the surface of the slightly anionic fiber of the pulp slurry.

[0126] Although not wishing to be bound by theory, the gelatinized starch composition, e.g., the essentially unreacted mixture of gelatinized starch and an aldehyde generating compounds, are incorporated into the pulp slurry of the wet end of the paper manufacturing process in an essentially unreacted form. After consolidation of the paper or paperboard web, exposure of the web, which comprises the gelatinized starch composition, to temperatures sufficient to dry the sheet under commercial paper drying conditions, which also induces degradation of the aldehyde generating compound, thereby releasing reactive aldehyde groups or glyoxal compounds having reactive aldehyde residues or a combination thereof. After release from the aldehyde generating compound, the reactive aldehyde groups or glyoxal compounds having reactive aldehyde residues react with functional groups, particularly hydroxyl and amine groups, from one or more starch molecules or moieties or the fiber surface to generate covalent bonds.

[0127] Gelatinized starch compositions provided by the invention may be prepared by any suitable method of forming an admixture of the aqueous starch solution and the aldehyde generating compound. Typically the aldehyde generating compound is added to the aqueous starch solution and the combined material is intimately mixed to form a substantially homogeneous composition. Although the mixing process may be carried out at room temperature, it is often desirable to gently heat the mixture while mixing to reduce the viscosity of the aqueous starch solution. In general, warming the mixture to between about 25° C. and about 40° C. is sufficient to reduce the viscosity without degradation of the aldehyde generating compound or initiating a reaction between the starch and the aldehyde generating compound. The blending or mixing of the starch and aldehyde generating compound is typically complete in less than 24 hours and is preferably complete in less than about 12, 8, or 6 hours. In particularly preferred methods of making the gelatinizes starch compositions of the invention the mixing or blending step is complete in between about 1 and about 3 hours.

[0128] The shelf life of the gelatinized starch composition is typically dependent upon, among other things, the concentration of the starch, the concentration of the aldehyde generating compound, the rate at which the starch will degrade back to its crystalline form and the rate at which the aldehyde generating compound reacts with the starch at ambient or storage temperature.

[0129] The shelf-life measurements as used herein refer to the ability of the gelatinized starch composition to be transferred between storage and reactor vessels by traditional pumping means used in the papermaking industry. The gelatinized starch compositions of the invention comprising of at least one aldehyde generating compound or glyoxal releasing compound, has generally reached its' shelf life limit when the gelatinized starch composition can not be pumped from the storage vessel. A typical starch composition can be defined to be transferable if its viscosity is less than 15000 cps.

[0130] Stability of the gelatinized starch compositions of the invention are typically measured based upon the viscosity measurement of the composition. In general, any gelatinized starch composition of the invention which has a viscosity of 10,000 cPs or less after about one (1), two (2), or three (3) weeks, or more preferably after one month, is considered to have sufficient stability. Viscosity of the gelatinized starch compositions are routinely measured suing a Brookfield viscometer having a #4 spindle rotating at 10 or 20 rpm.

[0131] In preferred methods of making paper provided by the present invention the aldehyde generating compound or

the glyoxal releasing compound is generally a polar, non-ionic compound and, consequently, has minimal affinity for direct interacting with fiber present in the pulp slurry which is weakly anionic. Applicants have surprisingly discovered that the preferred aldehyde generating compound or glyoxal releasing compounds interact with cationic starch molecules and are localized to the fiber of the paper slurry when the cationic starch adheres to the fiber surface. Although not wishing to be bound by theory, the interaction between the cationic starch and the aldehyde generating compound or glyoxal releasing compound is likely due, in part, to dipole or electrostatic interactions between the starch and the aldehyde generating compound or glyoxal releasing compound.

[0132] As used herein, "alkyl" is intended to include both branched and straight-chain saturated aliphatic hydrocarbon groups, having the specified number of carbon atoms. Examples of alkyl include, but are not limited to, methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, and s-pentyl. Preferred alkyl groups are C_{1-6} alkyl groups. Especially preferred alkyl groups are methyl, ethyl, propyl, butyl, and 3-pentyl. The term C_{1-4} alkyl as used herein includes alkyl groups consisting of 1 to 4 carbon atoms, which may contain a cyclopropyl moiety. Suitable examples are methyl, ethyl, and cyclopropylmethyl. The term "alkyl" is also intended to include cycloalkyl and cycloalkylalkyl groups where there term "cycloalkyl" is used as defined herein.

[0133] "Cycloalkyl" is intended to include saturated ring groups, having the specified number of carbon atoms, such as cyclopropyl, cyclobutyl, cyclopentyl, or cyclohexyl. Cycloalkyl groups typically will have 3 to about 8 ring members.

[0134] "Alkenyl" is intended to include hydrocarbon chains of either a straight or branched configuration comprising one or more unsaturated carbon-carbon bonds, which may occur in any stable point along the chain, such as ethenyl and propenyl. Alkenyl groups typically will have 2 to about 8 carbon atoms, more typically 2 to about 6 carbon atoms.

[0135] "Alkynyl" is intended to include hydrocarbon chains of either a straight or branched configuration comprising one or more carbon-carbon triple bonds, which may occur in any stable point along the chain, such as ethynyl and propynyl. Alkynyl groups typically will have 2 to about 8 carbon atoms, more typically 2 to about 6 carbon atoms.

[0136] "Alkoxy" represents an alkyl group as defined above with the indicated number of carbon atoms attached through an oxygen bridge. Examples of alkoxy include, but are not limited to, methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, 2-butoxy, t-butoxy, n-pentoxy, 2-pentoxy, 3-pentoxy, isopentoxy, neopentoxy, n-hexoxy, 2-hexoxy, 3-hexoxy, and 3-methylpentoxy. Alkoxy groups typically have 1 to about 8 carbon atoms, more typically 1 to about 6 carbon atoms.

[0137] In the papermaking process wood pulp is prepared, bleached if required, cleaned, and run through a series of beaters or refiners until it is a fine slush. At this point fillers and other additives, such as the gelatinized starch compositions of the invention, can be mixed in. When preparation is complete, the slush is pumped onto a fast-moving wire screen where it becomes consolidated into a continuous web or sheet of paper or paperboard.

[0138] As the consolidating web travels with the moving wire, excess water is drained away leaving a crude paper or paperboard sheet. The sheet is then squeezed between rollers or presses to remove some of the remaining water and to ensure uniform thickness and smoothness. Finally, the web is run over a series of heated rollers or heating devices to remove most of the remaining water. The paper may be "finished" in any number of ways, including but not limited to, surface treatments, calendaring, or coating. The finished paper is spooled onto 'parent rolls' termed the reel.

EXAMPLES

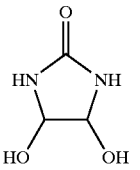
[0139] The present invention is further illustrated by the following examples which should not be construed as limiting in any way. The contents of all cited references (including literature references, issued patents, published patent applications) as cited throughout this application are hereby expressly incorporated by reference. The practice of the present invention will employ, unless otherwise indicated, conventional techniques, which are within the skill of the art. Such techniques are explained fully in the literature.

[0140] In the following example, laboratory handsheets were prepared using the MK sheet forming device in semi-automatic mode. Pulp was beaten to 300 CSF (Canadian Standard Freeness) using a laboratory beater. Additions were made to a 1% slurry of the pulp prior to addition to the headbox. Sheets (12×12") were formed using conventional practice, pressed, and dried at 120° C. using 2 passes through a felted rotating cylinder dryer. A pass is one rotation around the heated drum. The speed of this rotation is adjustable. For this study the rotation took 1 minute. The pulp slurries were prepared in ordinary tap water without pH adjustment. Old Corrugated Containers (OCC) was obtained from commercial box clippings.

Example 1

Preparation of a Mixture of 4,5-dihydroxy-imidazolidin-2-one and at Least One Aldehyde Blocking Compound

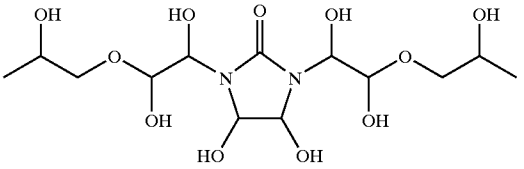
[0141] A 1000 ml flask was charged with glyoxal (40% in water, 145 grams, 1 mole) and the contents of the flask were stirred and warmed to 55° C. Urea (50% in water, 120 grams, 1 mole) was added to the stirred glyoxal solution over four hours at 55° C. To this mixture propylene glycol (38 grams, 0.5 moles) and a catalytic amount of sulfuric acid (98%, typically about 1 gram) was added. The reaction mixture was then heated to 70° C. for two hours to generate the product, of which the predominant reaction produce had the structure, as follows:



Example 2

Preparation of a Cyclic Glyoxal with Pendant Blocked Glyoxal Residues

[0142] A 1000 ml flask was charged with glyoxal (40% in water, 435 grams, 3 moles) and the contents of the flask were stirred and warmed to 55° C. Urea (50% in water, 120 grams, 1 mole) was added to the stirred glyoxal solution over two hours at 55° C. A catalytic amount of sulfuric acid (98%, typically about 1 gram) was added to the reaction mixture to accelerate the cyclization reaction. The reaction mixture was allowed to stir for four hours and then propylene glycol (152 grams, 2 moles) was added. The reaction mixture was then heated to 70° C. for two hours to generate the product, of which the predominant reaction produce had the structure, as follows:



Example 3

Dry Strength Evaluation of Paper Manufactured with a Gelatinized Starch Composition Comprising the Compound of Example 1 as the Glyoxal Releasing Compound

[0143] A handsheet study demonstrating strength improvements included one handsheet set prepared without a starch additive and three sets of sheets with different starch compositions. Handsheets are 15 gm (12 in×12 in). Sample 3A was a control OCC furnish with no additives. Sets 3B thru 3D were made with the identical furnish and conditions but a different starch additive was used in each set.

[0144] Set 3B contained a cationic pregelatinized potato starch (Penford PAR 6048AR, available from Penford Products, Inc.), at 10 lb/ton and is referred to herein as the "starch only" control. Set 3C was prepared with a gelatinized starch composition comprising a mixture of Penford PAR 6048AR and the glyoxal releasing compound provided in Example 1. The mixture was prepared by mixing the glyoxal releasing compound into the Penford PAR 6048AR (25%) at 32° C. over 1 hour with agitation. The resulting mixture had a solids content of 23.7% by weight.

[0145] Set 3D was prepared using the same gelatinized starch composition as was used in Set 3C except that the gelatinized starch composition was prepared by mixing the glyoxal releasing compound from Example 1 into a Penford PAR 6048AR at 90° C. over 30 minutes with agitation (pre-reaction process). In both 3C and 3D the glyoxal releasing compound was blended into Penford PAR 6048AR at 10% by weight dry on dry. The combination was added to the OCC slurry at 10 lb/ton.

TABLE I

Sample	Description	Dry Tensile	Shelf-Life
3A	fiber control	46.04	NA
3B	starch control	47.26	6 months
3C	cold blend	57.65	3 months
3D	pre-reacted	55.72	3 weeks

[0146] The results demonstrate that the dry strength of the paperboard was improved when the glyoxal releasing compound was added to the starch. Performance in terms of strength development and stability are best when the material is added to the starch under mild conditions (example 3C). Moreover, treatment of the gelatinized starch composition under the conditions of the pre-reaction process reduces the stability of the starch composition.

Example 4

Dry Strength Evaluation of Paper Manufactured with a Gelatinized Starch Composition Comprising the Compound of Example 2 as the Glyoxal Releasing Compound

[0147] A handsheet study demonstrating strength improvements included one handsheet set prepared without a starch additive and three sets of sheets with different starch compositions. Handsheets are 15 gm (12 in×12 in). Sample 4A was a control OCC furnish with no additives. Sets 4B thru 4D were made with the identical furnish and conditions but a different starch additive was used in each set.

[0148] Set 4B contained a cationic pregelatinized potato starch (Penford PAR 6048AR), at 10 lb/ton and is referred to herein as the "starch only" control. Set 4C was prepared with a gelatinized starch composition comprising a mixture of Penford PAR 6048AR and the glyoxal releasing compound provided in Example 2. The mixture was prepared by mixing the glyoxal releasing compound into the Penford PAR 6048AR (25%) at 32° C. over 1 hour with agitation. The resulting mixture had a solids content of 23.7% by weight.

[0149] Set 4D was prepared using the same gelatinized starch composition as was used in Set 4C except that the gelatinized starch composition was prepared by mixing the glyoxal releasing compound from Example 2 into Penford PAR 6048AR at 90° C. over 30 minutes with agitation (pre-reaction process). In both 4C and 4D the glyoxal releasing compound was blended into Penford PAR 6048AR at 10% by weight dry on dry. The combination was added to the OCC slurry at 10 lb/ton.

TABLE II

Sample	Description	Dry Tensile	Shelf-Life
4A	fiber control	46.04	NA
4B	starch control	47.26	6 months
4C	cold blend	52.47	1.5 days
4D	pre-reacted	ND	<1 hour

[0150] The results demonstrate that the dry strength of the paperboard was improved when the glyoxal releasing compound of Example 2 was added to the gelatinized starch

composition. Performance in terms of strength development and stability were best when the material was added to the starch under the mild conditions (example 4C). Treatment of the gelatinized starch composition with harsh conditions, such as those of set 4D, resulted in a gelatinized starch composition that was not usable for use in commercial applications, due in part to a short shelf life.

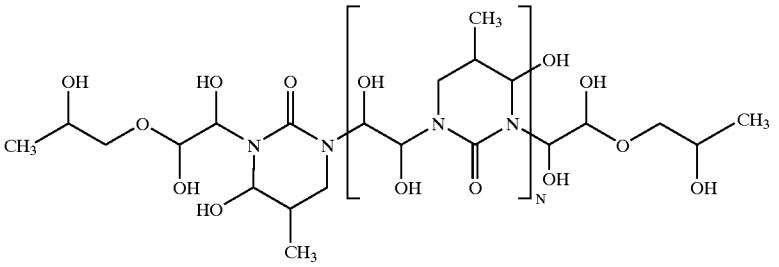
Example 5

Preparation of Cyclic Amide with Pendent Blocked Glyoxal Units

[0151] Sodium bicarbonate (7.5 grams) was introduced into a sealed nitrogen filled round bottom flask fixed with heating, cooling, reflux, distillation, pH probe, temperature probe and constant pressure addition apparatus. Formaldehyde (37% in water, 172 grams, 2 moles) was then added to the flask. Propionaldehyde (116 grams, 2 moles) was then slowly added to the reaction mixture over 2 hours at 30° C. Upon complete addition of the propionaldehyde, the reaction solution was heated to 45° C. for 4 hours. Urea (120 grs (2 moles)) was then added and the temperature of the reaction mixture increased to 60° C. for 2 hours. Residual raw materials and a small amount of reaction by-products were then removed from the reaction flask by vacuum distillation. Sulfuric acid (98%, 6.25 grams) was added to the material remaining in the flask after distillation and the reaction mixture was held at 60° C. for 4 hours.

[0152] Glyoxal (40% by weight in water; 290 grams, 2 moles) and propylene glycol (152 grams, 2 moles) were added sequentially at 55° C. to the reaction mixture. The reaction mixture was allowed to stir for an hour after complete addition of each reagent, e.g., glyoxal and propylene glycol.

[0153] The reaction mixture was returned to room temperature and the pH was adjusted to about 6.5 by addition of sodium bicarbonate. The predominate glyoxal releasing compound formed by the reaction is represented by the structure, as follows:



Example 6

Dry Strength Evaluation of Paper Manufactured with a Gelatinized Starch Composition Comprising the Compound of Example 5 as the Glyoxal Releasing Compound

[0154] A handsheet study demonstrating strength improvements included one handsheet prepared without a starch additive and three sets of sheets with different starch compositions. Handsheets are 15 gm (12 in×12 in). Sample 6A was a control OCC furnish with no additives. Sets 6B thru 6D were made with the identical furnish and conditions but a different starch additive was used in each set.

[0155] Set 6B contained a cationic pregelatinized potato starch (Penford PAR 6048AR), at 10 lb/ton and is referred to herein as the "starch only" control. Set 6C was prepared with a gelatinized starch composition comprising a mixture of Penford PAR 6048AR and the glyoxal releasing compound provided in Example 5. The mixture was prepared by mixing the glyoxal releasing compound into the Penford PAR 6048AR (25%) at 32° C. over 1 hour with agitation. The resulting mixture had solids of 23.7%.

[0156] Set 6D was prepared using the same gelatinized starch composition as was used in Set 6C except that the gelatinized starch composition was prepared by mixing the glyoxal releasing compound from Example 5 into Penford PAR 6048AR at 90° C. over 30 minutes with agitation (pre-reaction process). In both 6C and 6D the glyoxal releasing compound was blended into Penford PAR 6048AR at 10% by weight dry on dry. The combination was added to the OCC slurry at 10 lb/ton.

TABLE III

Sample	Description	Dry Tensile	Shelf-Life
6A	fiber control	46.04	NA
6B	starch control	47.26	6 months
6C	cold blend	57.47	1 month
6D	pre-reacted	56.41	5 days

Example 7

Production Scale Paper Manufactured Using Gelatinized Starch Composition in Which the Glyoxal Releasing Compound is the Compound Provided by Example 1

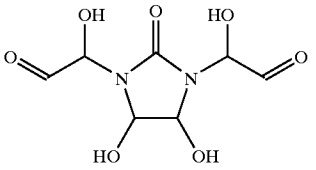
[0157] A 10 tote trial of a gelatinized starch composition was prepared by mixing the comprising a glyoxal releasing compound provided by Example 1 and Penford PAR 6048AR cationic potato starch (7%:93% by weight of glyoxal releasing compound:starch) to give a final combined concentration of 21% (less than 3000 cps). The gelatinized starch composition was added to the paper making process at several locations in the wet end of the paper making process, such as the suction side of the machine chest fan pump and the suction side of the pressure screen. During this trial the average dosage rate of the gelatinized starch composition was about 10 pounds per ton.

[0158] The paper manufacturing method using the gelatinized starch composition having a glyoxal releasing compound provided by Example 1 provides the following benefits: (1) reduced the basis weight of the paperboard by approximately 1.5%; (2) increased the speed of the machine by approximately 6%; (3) maintained the ring crush and Mullen test parameters of the paperboard while the speed was increased and the basis weight was reduced; (4) increased drainage from the consolidated web; (5) reduced filler machine chest turbidity; and (6) reduced white water turbidity.

Example 8

Preparation of a Cyclic Glyoxal Compound with Pendant Glyoxal Residues and No Aldehyde Blocking

[0159] A 1000 ml flask was charged with glyoxal (40% in water, 435 grams, 3 moles) and sulfuric acid (98%, 2 grams) and was stirred and warmed to 65° C. Urea (50% in water, 120 grams, 1 mole) was added to the stirred glyoxal solution over four hours at 65° C. The reaction mixture was held for two hours at 70° C. to generate the product, of which the predominant reaction product had the structure, as follows:



Example 9

Demonstration of Stability for glyoxal Releasing Compounds in a Self-Retaining Starch Solution

[0160] Penford PAR 6048AR cationic potato starch was blended with the glyoxal releasing compounds taken from example 1, 5, and 8. In addition, unreacted/unblocked glyoxal was used as a comparison. The blending was done at ambient temperature and for 30 minutes. The blend ratio and starch solids are listed in Table IV. A Brookfield RV viscometer (spindle #5/10 rpm/25° C.) was used to measure the viscosity.

TABLE IV

	10% Active Starch Solids 15% Active crosslinker			
Crosslinker Viscosity	Glyoxal	Example #1	Example #8	Example #5
2 Hours	Gel (0.5 hr)	300 cPs	Gel (0.5 hr)	350 cPs
4 Hours	Gel	300 cPs	Gel	300 cPs
6 Hours	Gel	300 cPs	Gel	300 cPs
8 Hours	Gel	300 cPs	Gel	300 cPs
24 Hours	Gel	300 cPs	Gel	300 cPs

[0161] The results in Table IV demonstrate that the blocked aldehyde containing compounds of type demonstrated in Examples 1 and 5 can produce stable mixtures with starch while unblocked aldehyde containing compounds, like that of example 8, and glyoxal will not produce stable mixtures with starch.

[0162] The disclosures of all articles and references mentioned in this application, including patents, are incorporated herein by reference.

[0163] The invention and the manner and process of making and using it, are now described in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains, to make and use the same. It is to be understood that the foregoing describes preferred embodiments of the present invention and that modifications may be made therein without departing from the spirit or scope of the present invention as set forth in the claims. To particularly point out and distinctly claim the subject matter regarded as invention, the following claims conclude this specification.

What is claimed is:

1. A method for manufacturing paper or paperboard sheet with increased strength, the method comprising the steps of:

providing a fiber slurry suitable for use in making paper or paperboard;

incorporating a gelatinized starch composition into the fiber slurry, wherein the gelatinized starch composition comprises:

gelatinized starch; and

an aldehyde generating compound capable of forming at least two or more covalent bonds to functional groups present in the starch or fiber when the aldehyde generating compound is heated above an activation temperature;

forming the paper or paperboard sheet;

heating the paper or paperboard sheet at a temperature above the activation temperature of the aldehyde generating compound which is sufficient to dry the paper or paperboard sheet.

2. The method of claim 1, wherein a paper sheet is prepared by the method of manufacture.

3. The method of claim 1, wherein a paperboard sheet is prepared by the method of manufacture.

4. The method of claim 1, wherein the starch is self-retaining.

5. The method of claim 4, wherein the starch is a net cationic starch.

6. The method of claim 4, wherein the starch is pregelatinized self-retaining starch selected from potato, corn or wheat starch.

7. The method of claim 1, wherein the gelatinized starch composition comprises between 0.5% to 50% aldehyde generating compound based on the dry weight of the starch and aldehyde generating compound.

8. The method of claim 1, wherein the aldehyde generating compound reacts with starch or gelatinized starch with a rate sufficiently slow to permit storage of the composition for at least one day at room temperature.

9. The method of claim 8, wherein the aldehyde generating compound reacts with starch or gelatinized starch at a sufficiently slow rate to permit storage of the composition for at least one week at room temperature.

10. The method of claim 8, wherein the aldehyde generating compound reacts with starch or gelatinized starch at a sufficiently slow rate to permit storage of the composition for at least three weeks at room temperature.

11. The method of claim 1, wherein the gelatinized starch composition further comprises at least one aldehyde blocking compound capable of blocking aldehyde residues.

12. The method of claim 11, wherein the aldehyde blocking compound loading is at least 10 molar % of the aldehyde generating compound.

13. The method of claim 11, wherein the aldehyde blocking compound is selected from the group consisting of C_{1-20}alcohols, C_{2-20}alkylene glycols, and C_{1-20}alkylamines.

14. The method of claim 11, wherein the aldehyde blocking compound is selected from the group consisting of methanol, ethanol, propanol, ethylene glycol, glycerin, propylene glycol and urea.

15. The method of claim 1, wherein the aldehyde generating compound is a glyoxal releasing compound.

16. The method of claim 15, wherein the glyoxal releasing compound is a reaction product of at least one molar equivalent of glyoxal with between about 0.25 and about 5 molar equivalents of one or more stabilizing agents.

17. The method of claim 16, wherein the glyoxal releasing compound thermally degrades at the temperature sufficient to dry paper or paperboard thereby releasing one or more equivalents of glyoxal.

18. The method of claim 17, wherein the thermally released glyoxal forms crosslinks between two starch moieties or between a starch moiety and fiber by reacting with functional groups of the starch moiety or fiber to form covalent bonds.

19. The method of claim 16, wherein the glyoxal releasing compound is a reaction product of

at least one molar equivalent of glyoxal; and

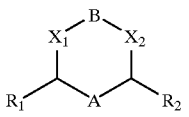
between about 0.5 and about 5 molar equivalents of stabilizing agents selected from the group consisting of optionally substituted urea, optionally substituted thiourea, optionally substituted imidazolidin-2-one, and optionally substituted tetrahydro-pyrimidin-2-one.

20. The method of claim 11, wherein the aldehyde generating compound is a reaction product of

at least one molar equivalent of glyoxal; and

between about 1 and about 3 molar equivalent of stabilizing agents selected from the group consisting of urea, thiourea, 4,5-dihydroxy-imidazolidin-2-one, and 4-hydroxy-5-(C_{1-10}-alkyl)-tetrahydro-pyrimidin-2-one.

21. The method of claim 19, wherein the glyoxal releasing compound is a compound according to Formula I:



I

wherein

A is an optionally substituted methylene group, an optionally substituted C_{2-4}alkylene group, or a single bond;

B is carbonyl, thiocarbonyl, or an optionally substituted 1,2-ethylene residue;

X_1 and X_2 are independently selected from the group consisting of oxygen and NR_3;

R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, optionally substituted C_{1-20}alkyl, optionally substituted C_{1-20}alkoxy, optionally substituted urea, optionally substituted thiourea, or

R_1 and R_2, taken in combination, form a N,N'-divalent urea;

R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, optionally substituted C_{1-20}alkyl, and blocked glyoxal residues, where the blocked glyoxal residue is a 1-hydroxy-2-(protected aldehyde residue)-ethan-1-yl group; and

wherein the aldehyde generating compound according to Formula I thermally degrades to generate at least one equivalent of glyoxal when heated above an activation temperature.

22. The method of claim 21, wherein the aldehyde generating compound is a glyoxal releasing compound.

23. The method of claim 22, wherein

R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, methanol, ethanol, urea, or

R_1 and R_2, taken in combination, form a N,N'-divalent urea;

R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, methyl, and ethyl, or

R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

24. The method of claim 22, wherein

X_1 and X_2 are NR_3;

A is a single bond;

B is a carbonyl or thiocarbonyl group; and

R_1 and R_2 are independently selected from hydroxyl, C_{1-6}-alkoxy, or blocked glyoxal residues.

25. The method of claim 22, wherein

X_1 and X_2 are NR_3;

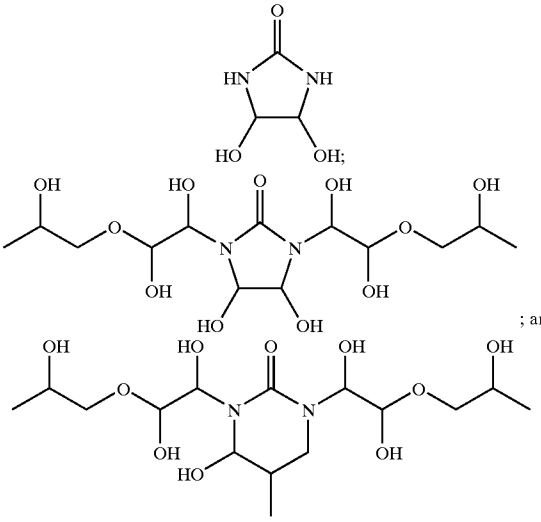
A is a 1,1-C_{1-6}alkylene group;

B is a carbonyl or thiocarbonyl group;

R_1 and R_2 are independently selected from hydrogen, hydroxyl, C_{1-6}-alkoxy, or blocked glyoxal residues; and

R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

26. The method of claim 22, wherein the glyoxal releasing compound comprises at least one compound selected from the group consisting of compounds of the formulae:



; and

.

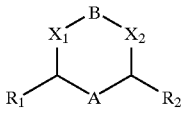
27. The method of claim 1, wherein the gelatinized starch composition further comprises a cationic starch containing at least one ammonium salt.

28. A gelatinized starch composition for use strengthening paper or paperboard, the composition comprising:

a self-retaining gelatinized starch;

at least one aldehyde blocking compound capable of blocking aldehyde residues; and

an aldehyde generating compound according to the Formula I:



I

wherein

A is an optionally substituted methylene group, an optionally substituted C_{2-4}alkylene group, or a single bond;

B is carbonyl, thiocarbonyl, or an optionally substituted 1,2-ethylene residue;

X_1 and X_2 are independently selected from the group consisting of oxygen and. NR_3;

R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, optionally substituted C_{1-20}alkyl, optionally substituted C_{1-20}alkoxy, optionally substituted urea, optionally substituted thiourea, or

R_1 and R_2, taken in combination, form a N,N'-divalent urea;

R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, optionally substituted C_{1-20}alkyl, and blocked glyoxal residues, where the blocked glyoxal residue is a 1-hydroxy-2-(protected aldehyde residue)-ethan-1-yl group;

wherein the aldehyde generating compound according to Formula I thermally degrades to generate at least one equivalent of aldehyde when heated above an activation temperature; and

wherein the aldehyde blocking compound loading is at least 10 molar % of the aldehyde generating compound.

29. The gelatinized starch composition of claim 28, wherein the aldehyde generating compound is a glyoxal releasing compound.

30. The gelatinized starch composition of claim 29, wherein the glyoxal releasing compound reacts with starch or gelatinized starch with a rate sufficiently slow to permit storage of the composition for at least one day at room temperature.

31. The gelatinized starch composition of claim 29, wherein the glyoxal releasing compound reacts with starch or gelatinized starch at a sufficiently slow rate to permit storage of the composition for at least one week at room temperature.

32. The gelatinized starch composition of claim 29, wherein the glyoxal releasing compound reacts with starch or gelatinized starch at a sufficiently slow rate to permit storage of the composition for at least three weeks at room temperature.

33. The gelatinized starch composition of claim 29, wherein the glyoxal releasing compound is capable of forming at least two or more covalent bonds to functional groups present in the starch or fiber when the glyoxal releasing compound is heated above an activation temperature.

34. The gelatinized starch composition of claim 29, wherein the starch is a cationic starch.

35. The gelatinized starch composition of claim 29, wherein the starch is selected from potato, corn or wheat starch.

36. The gelatinized starch composition of claim 29, wherein the aldehyde blocking compound is selected from the group consisting of C_{1-20}alcohols, C_{2-20}alkylene glycols, and C_{1-20}alkylamines.

37. The gelatinized starch composition of claim 29, wherein the aldehyde blocking compound is selected from the group consisting of methanol, ethanol, propanol, ethylene glycol, and propylene glycol.

38. The gelatinized starch composition of claim 29, wherein

R_1 and R_2 are independently selected from the group consisting of hydrogen, hydroxyl, methanol, ethanol, urea, or

R_1 and R_2, taken in combination, form a N,N'-divalent urea;

R_3 is independently selected at each occurrence of R_3 from the group consisting of hydrogen, methyl, and ethyl, or

R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-

yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

39. The gelatinized starch composition of claim 29, wherein

X_1 and X_2 are NR_3;

A is a single bond;

B is a carbonyl or thiocarbonyl group; and

R_1 and R_2 are independently selected from hydroxyl, C_{1-6}alkoxy, or stabilized glyoxal residues.

40. The gelatinized starch composition of claim 29, wherein

X_1 and X_2 are NR_3;

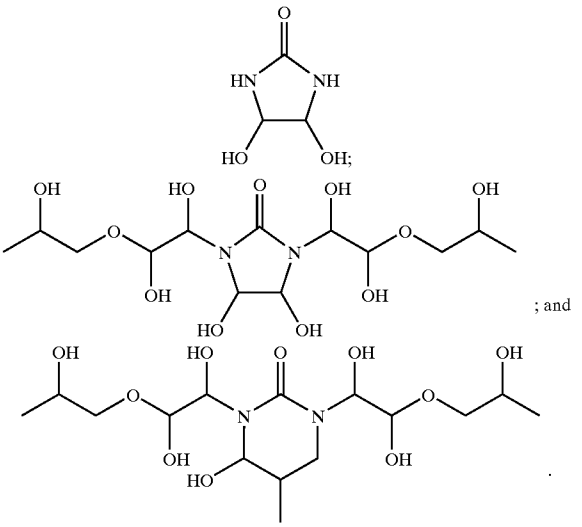
A is a 1,1-C_{1-6}alkylene group;

B is a carbonyl or thiocarbonyl group;

R_1 and R_2 are independently selected from hydrogen, hydroxyl, C_{1-6}alkoxy, or stabilized glyoxal residues; and

R_3 is a blocked glyoxal residue selected from the group consisting of 1,2-dihydroxy-2-(C_{1-4}-alkoxy)-ethan-1-yl, 1,2-dihydroxy-2-(3-hydroxypropoxy)-ethan-1-yl, and 1,2-dihydroxy-2-(2-hydroxypropoxy)-ethan-1-yl.

41. The gelatinized starch composition of claim 29, wherein the glyoxal releasing compound comprises at least one compound selected from the group consisting of is compounds of the formulae:



; and

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