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(54) Title: METHOD OF MODIFYING STARCH FOR INCREASED PAPER MACHINE RETENTION AND DRAINAGE PERFORMANCE

(57) Abstract: A method of modifying starch with metal silicates, and the use of the modified starch in the preparation of cellulosic fiber compositions. The method further relates to cellulosic fiber compositions, such as paper and paperboard, which incorporate the starch modified with metal silicates.



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METHOD OF MODIFYING STARCH FOR INCREASED PAPERMACHINE RETENTION AND DRAINAGE PERFORMANCE

FIELD OF THE INVENTION

[0001] The present invention relates to modifying starch with metal silicates, and the use of the modified starch in the preparation of cellulosic fiber compositions. The present invention further relates to cellulosic fiber compositions, such as paper and paperboard, which incorporate the starch modified with metal silicates.

BACKGROUND OF THE INVENTION

[0002] The making of cellulosic fiber sheets, particularly paper and paperboard, includes the following: 1) producing an aqueous slurry of cellulosic fiber; which may also contain inorganic mineral extenders or pigments; 2) depositing this slurry on a moving papermaking wire or fabric; and 3) forming a sheet from the solid components of the slurry by draining the water.

[0003] The foregoing is followed by pressing and drying the sheet to further remove water. Organic and inorganic chemicals are often added to the slurry prior to the sheet-forming step to make the papermaking method less costly, more rapid, and/or to attain specific properties in the final paper product.

[0004] The paper industry continuously strives to improve paper quality, increase productivity, and reduce manufacturing costs. Chemicals are often added to the fibrous slurry before it reaches the papermaking wire or fabric, to improve the drainage/dewatering and solids retention; these chemicals are called retention and/or drainage aids.

[0005] Drainage or dewatering of the fibrous slurry on the papermaking wire or fabric is often the limiting step in achieving faster method speeds. Improved dewatering can also result in a dryer sheet in the press and dryer sections, resulting in reduced energy or steam consumption. Yet further, this is the stage in the papermaking method that determines many sheet final properties.

[0006] Papermaking retention aids are used to increase the retention of fine furnish solids in the web during the turbulent method of draining and forming the paper web. Without adequate retention of the fine solids, they are either lost to the method effluent or accumulate to high levels in the recirculating white water loop, potentially causing deposit buildup. Additionally, insufficient retention increases the papermakers' cost due to loss of additives intended to be adsorbed on the fiber to provide the respective paper opacity, strength, or sizing property.

[0007] Cationic starch is utilized extensively in the paper industry. It is introduced into the pulp slurry to increase interfiber bonding and to obtain paper strength properties, to emulsify synthetic internal sizing agents, such as alkenyl succinic anhydride (ASA), or to provide drainage.

[0008] Metal silicates, which include sodium silicate, potassium silicate, and sodium metasilicate, are commodity chemicals utilized widely in many industries, including paper and water treatment.

[0009] In US Patent 5,185,206, Rushmere teaches an improved drainage aid and retention aid for papermaking which is added to an aqueous paper furnish containing pulp and which comprises a silicated cationic starch composition which is a dry solid which contains from about 1 to 25 wt % silica and consists essentially of granules of a cationized starch having the silica in the form of a water soluble polysilicate microgel deposited on the surfaces thereof and, optionally, the composition further containing discreet agglomerates of silica microgels in admixture with the silicated starch granules. The one-component product is a dry solid which offers convenience and economy over colloidal silica combinations because shipping large quantities of water can be avoided. In practicing the invention, it is preferred that as much microgel as possible be deposited onto the surface of each starch granule. Thereby, optimum redispersion of the microgels will be achieved when the starch is subsequently heated in water just prior to being used.

[0010] It has been unexpectedly discovered that the addition of metal silicate to cationic starch provides a remarkable increase in retention and drainage performance.

SUMMARY OF THE INVENTION

[0011] This invention describes a method for improving the retention and drainage properties during the papermaking process by the addition of a cationic or amphoteric polysaccharide or polysaccharide derivative that has been modified with a metal silicate.

[0012] The present method also provides for a method of modifying a cationic or amphoteric polysaccharide or polysaccharide derivative by the addition of a metal silicate.

[0013] The present invention also provides for a cationic or amphoteric polysaccharide or polysaccharide derivative modified with a metal silicate

[0014] In one embodiment of the invention the cationic or amphoteric polysaccharide or polysaccharide derivative is a cationic or amphoteric starch.

[0015] Also disclosed is a papermaking process comprising adding to a papermaking slurry, at least one polysaccharide or polysaccharide derivative, wherein the polysaccharide or polysaccharide derivative has been modified with at least one metal silicate, wherein the at least one polysaccharide or polysaccharide derivative is selected from the group consisting of polysaccharide derivatives containing a cationic nitrogen group, a blend of cationic and anionic polysaccharides and combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0016] It has been discovered that the addition of metal silicate to cationic starch will provide a dramatic increase in the drainage. Best results are obtained when the metal silicate is added to the starch after the starch has been cooked. The metal silicate can be added while the starch is still at an

elevated temperature or after the starch has been cooled to ambient temperatures. Improved retention and drainage performance has also been observed with adding the metal silicate to the water prior to adding the starch and cooking. In one embodiment of the invention the metal silicate is sodium silicate. The metal silicate may also be potassium silicate or sodium metasilicate.

[0017] The materials utilized in the method of the invention include cellulosic pulp and at least one starch modified with a metal silicate. There can also be employed one or more additional materials, including, but not limited to, additional unmodified starch, filler, inorganic or organic coagulant, conventional flocculant, and at least one organic or inorganic drainage aid.

[0018] In one embodiment of the invention the cationic or amphoteric polysaccharide or polysaccharide derivative is a cationic or amphoteric starch.

[0019] The order in which the different materials are introduced into the method of the invention is not limited to that set forth in the preceding discussion, but will generally be based on practicality and performance for each specific application.

[0020] Suitable cellulosic fiber pulps for the method of the invention include conventional papermaking stock such as traditional chemical pulp. For instance, bleached and unbleached sulfate pulp and sulfite pulp, mechanical pulp such as groundwood, thermomechanical pulp, chemi-thermomechanical pulp, recycled pulp such as old corrugated containers, newsprint, office waste, magazine paper and other non-deinked waste, deinked waste, and mixtures thereof, may be used.

[0021] Fillers are used in papermaking. Filler provides optical properties to the cellulosic product. It provides opacity and brightness to the finished sheet, and improves its printing properties. Fillers which are suitable include calcium carbonate (both naturally occurring ground carbonate and synthetically produced precipitated carbonate), titanium oxide, talc, clay, and gypsum. The amount of filler employed can be that which results in a cellulosic

product of up to about 50 weight percent filler, based on the dry weight of the pulp.

[0022] Coagulants are utilized to enhance retention and drainage. Coagulants may be either inorganic or organic. The most common inorganic coagulant is an alumina species. Suitable examples include, but are not limited to, technical grade aluminum sulfate (alum), polyaluminum chloride, polyhydroxy aluminum chloride, polyhydroxy aluminum sulfate, sodium aluminate, and the like. The organic coagulant is typically a synthetic, polymeric material. Suitable examples include, but are not limited to, polyamines, poly(amido amines), polyDADMAC (poly(diallyldimethylammonium chloride)), polyethyleneimine, hydrolyzates and quaternized hydrolyzates of N-vinyl formamide polymers and copolymers, and the like.

[0023] Coagulants are generally employed in a proportion of from about 0.05 lb. per ton to about 50 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The coagulant concentration can be from about 0.5 lbs. per ton to about 20 lbs. per ton, and or from about 1 lb. per ton to about 10 lbs. per ton, of the pulp.

[0024] Ionic flocculants are conventionally used in the papermaking art.. Cationic, anionic, nonionic, and amphoteric flocculants--particularly, cationic, anionic, nonionic, and amphoteric polymers--can be used. Polymers suitable as flocculants include, but are not limited to, homopolymers of a nonionic ethylenically unsaturated monomer. Copolymers of monomers comprising two or more nonionic ethylenically unsaturated monomers can also be used, as can copolymers of monomers comprising at least one nonionic ethylenically unsaturated monomer and at least one cationic ethylenically unsaturated monomer and/or at least one anionic ethylenically unsaturated monomer. Suitable nonionic ethylenically unsaturated monomers include, but are not limited to, acrylamide; methacrylamide; N-alkylacrylamides, such as N-methylacrylamide; N,N-dialkylacrylamides, such as N,N-dimethylacrylamide; methyl acrylate; methyl methacrylate; acrylonitrile; N-vinyl methylacetamide; N-

vinyl methyl formamide; vinyl acetate; N-vinyl pyrrolidone; hydroxyalkyl(meth) acrylates such as hydroxyethyl(meth) acrylate or hydroxypropyl(meth) acrylate; mixtures of any of the foregoing and the like. Of the foregoing, acrylamide, methacrylamide, and the N-alkylacrylamides are preferred, with acrylamide being particularly preferred.

[0025] The cationic ethylenically unsaturated monomers which may be used include, but are not limited to, diallylamine, the (meth)acrylates of dialkylaminoalkyl compounds, the (meth)acrylamides of dialkylaminoalkyl compounds, the N-vinylamine hydrolyzate of N-vinylformamide, and the salts and quaternaries thereof. The N,N-dialkylaminoalkyl acrylates and methacrylates, and their acid and quaternary salts, are preferred, with the methyl chloride quaternary of N,N-dimethylaminoethylacrylate being particularly preferred.

[0026] Suitable anionic ethylenically unsaturated monomers include, but are not limited to, acrylic acid, methacrylic acid, and their salts; 2-acrylamido-2-methyl-propane sulfonate; sulfoethyl-(meth)acrylate; vinylsulfonic acid; styrene sulfonic acid; and maleic and other dibasic acids and their salts. Acrylic acid, methacrylic acid and their salts are preferred, with the sodium and ammonium salts of acrylic acid being particularly preferred.

[0027] Cationic polymer flocculants will generally contain one or more of the cationic monomers described above. The level of total cationic monomer, based upon molar concentrations, can range from about 1 to about 99%, preferably from about 2 to about 50%, and still more preferably from about 5 to about 40 mole % cationic monomer, with the remaining monomer being one of the previously described non-ionic monomers.

[0028] Anionic polymer flocculants will generally contain one or more of the anionic monomers described above. The level of total anionic monomer, based upon molar concentrations, will range from about 1 to about 99%, preferably from about 2 to about 50%, and still more preferably from about 5 to

about 40 mole % anionic monomer, with the remaining monomer being one of the previously described non-ionic monomers.

[0029] Amphoteric polymer flocculants will contain a combination of one or more of the described cationic and anionic monomers. Any combination of cationic and anionic monomer(s) can be used, provided at least one cationic and one anionic monomer are utilized. The polymer may contain an excess of cationic monomer, an excess of anionic monomer, or equivalent amounts of both cationic and anionic monomers. The level of total ionic monomer, being the combined amount of both cationic and anionic monomers, based upon molar concentrations, will range from about 1 to about 99%, preferably from about 2 to about 80%, and still more preferably from about 5 to about 40 mole % ionic monomer, with the remaining monomer being one of the previously described non-ionic monomers. The flocculant can be employed, in a proportion of from about 0.01 lb. per ton to about 10 lbs. per ton of cellulosic pulp, based upon active polymer weight and on the dry weight of the pulp. The concentration of flocculant is more preferably from about 0.05 lb. per ton to about 5 lbs. per ton, and still more preferably from about 0.1 lb. per ton to about 1 lb. per ton, of the pulp.

[0030] In addition to the conventional flocculants, inorganic or organic drainage aids, known in the art as microparticles, micropolymers, organic microbeads, or associative polymers, may also be employed.

[0031] The inorganic microparticles employed include any of the materials selected from the group consisting of silica based particles, silica microgels, colloidal silica, silica sols, silica gels, polysilicates, polysilicate microgels, aluminosilicates, polyaluminosilicates, borosilicates, polyborosilicates and zeolites. The inorganic microparticle may also be a swellable clay, including, but not limited to, clays often referred to as hectorite, smectites, montmorillonites, nontronites, saponite, sauconite, hormites, attapulgitites and sepiolites.

[0032] The micropolymers or organic microbeads are crosslinked, cationic or anionic, polymeric, organic microparticles having an unswollen number average particle size diameter of less than about 750 nanometers and a crosslinking agent content of above about 4 molar parts per million based on the monomeric units present in the polymer and are generally formed by the polymerization of at least one ethylenically unsaturated cationic or anionic monomer and, optionally, at least one non-ionic comonomer in the presence of said crosslinking agent. One example of a micropolymer is Polyflex® (CIBA Corporation, Tarrytown, NY)

[0033] The associative polymer useful in the present invention can be described as a water-soluble copolymer composition, wherein the associative properties of the inverse emulsion anionic copolymer are provided by an emulsification surfactant chosen from diblock and triblock polymeric surfactants. The associative inverse emulsion anionic copolymer contains at least one nonionic polymer segment and at least one anionic polymer segment, and has a Huggins' constant (k') determined in 0.01 M NaCl greater than 0.75 and a storage modulus (G') in a 1.5 wt. % actives polymer solution at 4.6 Hz greater than 175 Pa. Examples of associative polymers include, but are not limited, to PerForm®9232 and PerForm® 7200 (Hercules Incorporated, Wilmington, DE)

[0034] Starch adds strength properties to the cellulose products, particularly dry strength by increasing inter-fiber bonding. Starch will also affect drainage properties. Starch is the common name for a polymer of glucose that contains alpha-1,4 linkages. Starch is a naturally occurring material; this carbohydrate can be found in the leaves, stems, roots and fruits of most land plants. The commercial sources of starch include, but are not limited to, the seeds of cereal grains (corn, wheat, rice, etc.), and certain roots (potato, tapioca, etc.). Starch is described by its plant source; reference would be made to, for example, corn starch, potato starch, tapioca starch, rice starch, and

wheat starch.. Starch can be considered to be a condensation polymer of glucose.

[0035] Generally starches consist of a mixture of two polysaccharide types: amylose, an essentially linear polymer, and amylopectin, a highly branched polymer. The relative amounts of amylose and amylopectin vary with the source, with the ratio of amylose to amylopectin typically being 17:83 for tapioca, 21:79 for potato, 28:72 for corn and 0:100 for waxy maize corn. Although these are the typical starch ratios found the present invention contemplates that any ratio of amylose to amylopectin can be useful in the present invention. For the purposes of this invention waxy maize is considered a type of corn starch.

[0036] Starch is synthesized by plants and accumulates in granules that are distinctive for each plant. Starch granules are separated from the plant through a milling and grinding process. The granules are insoluble in cold water and must be heated above a critical temperature in order for the granules to swell and rupture, allowing the polymer to dissolve in solution.

[0037] Starch can be modified to provide specific properties of value in selected applications. This includes modification to either or both the physical and chemical structure of the material. Physical modification includes reduction in molecular weight, which is most often achieved by hydrolysis. Such modified materials are often referred to as derivatized starch or starch derivatives.

[0038] The present invention modifies a cationic or amphoteric polysaccharide or polysaccharide with a metal silicate. The cationic or amphoteric polysaccharide or polysaccharide derivative is preferably a cationic or amphoteric starch or starch derivative.

[0039] Starches that may be used in the method of the invention include cationic and amphoteric starches. Suitable starches include those derived from corn, potato, wheat, rice, tapioca, and the like. Cationicity is imparted by the introduction of cationic groups, and amphotericity by the further introduction of anionic groups. For instance, cationic starches may be obtained

by reacting starch with tertiary amines or with quaternary ammonium compounds, e.g., dimethylaminoethanol and 3-chloro-2-hydroxypropyltrimethylammonium chloride. Cationic starches preferably have a cationic degree of substitution (D.S.)—i.e., the average number of cationic groups substituted for hydroxyl groups per anhydroglucose unit—of from about 0.01 to about 1.0, more preferably about 0.01 to about 0.10, more preferably about 0.02 to 0.04.

[0040] Amphoteric starches can be provided by adding anionic groups to cationic starches. Preferred amphoteric starches are those with a net cationicity. As an example, anionic phosphate groups can be introduced into cationic starches through reaction with phosphate salts or phosphate etherifying reagents. Where the cationic starch starting material is starch diethylaminoethyl ether, the amount of phosphate reagent employed in the modification preferably is that which will provide about 0.07-0.18 mole of anionic groups per mole of cationic groups.

[0041] Other amphoteric starches that may be used are those made by introduction of sulfosuccinate groups into cationic starches. This modification is accomplished by adding maleic acid half-ester groups to a cationic starch and reacting the maleate double bond with sodium bisulfite.

[0042] Cationic starch can also be etherified with 3-chloro-2-sulfopropionic acid, carboxyl groups can be introduced into starches by reaction with sodium chloroacetate or by hypochlorite oxidation, and propane sulfone can be employed to treat cationic starches to provide amphotericity.

[0043] Further useful amphoteric starches can be obtained by xanthation of diethylaminoethyl- and 2-(hydroxypropyl)trimethylammonium starch ethers.

Yet additionally, the modification can be extended by the introduction of nonionic or hydroxyalkyl groups from treatment with ethylene oxide or propylene oxide.

[0044] Starches that require gelatinizing or "cooking" at the use location, or pre-gelatinized, cold-water dispersion starches can be used. Starch granules are insoluble in water. The gelatinization of starch at elevated temperatures results in water penetrating the starch granule, rupturing the granule and releasing the starch molecule into solution. The release of the starch molecule into solution results in an increase in the solution viscosity. The starch is cooked by heating an aqueous solution of starch for 10 to 90 minutes at temperatures of 50° to 98° C until a thick, clear solution is obtained.

[0045] In some embodiments of the present invention aqueous solutions of starch are prepared at concentrations typically ranging from 1 to 5%. The Starch is added to cellulosic pulp, in a proportion of from about 1 lb. per ton to about 100 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The starch concentration is more preferably from about 2.5 lbs. per ton to about 50 lbs. per ton, and still more preferably from about 5 lbs. per ton to about 25 lbs. per ton, of the pulp. These weights do not include the weight of the metal silicate used to modify the starch. In the present invention the starch or a portion of the starch will be modified by metal silicate prior to being added to the cellulosic pulp.

[0046] Metal silicate is preferably employed, in the method of the invention, in a proportion of from about 0.1 lb. per ton to about 10 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The metal silicate concentration is more preferably from about 0.5 lbs. per ton to about 5 lbs. per ton, and still more preferably from about 1 lb. per ton to about 2 lbs. per ton, of the pulp.

[0047] The weight ratio of cationic starch to metal silicate (as SiO₂) can vary from 1:10 to 100:1 or can vary for 1:1 to 50:1. The preferred weight ratio is from about 20:1 to about 2:1, or from 15:1 to 2:1, or from 10:1 to 2:1 or from 10:1 to 3:1.

[0048] Other polysaccharides may also be employed for modification with metal silicates. These include, but are not limited to, guar, cellulose

derivatives such as hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, chitin and the like. The other polysaccharides may be unsubstituted, or substituted with cationic, anionic, or combined cationic or anionic moieties. These polysaccharides are in a proportion of from about 1 lb. per ton to about 100 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp, preferably from about 2.5 lbs. per ton to about 50 lbs. per ton, and still more preferably from about 5 lbs. per ton to about 25 lbs. per ton, of the pulp. These weights do not include the weight of the metal silicate used to modify the polysaccharide.

[0049] The metal silicate can be any of the alkali silicate commonly utilized, including, for example sodium silicate, aka "water glass", potassium silicate, and sodium metasilicate or any combination of the metal silicates. Sodium silicate can vary in the $\text{SiO}_2\text{:Na}_2\text{O}$ weight ratio, which is controlled during manufacture by the ratio of the two reactants. The ratio of $\text{SiO}_2\text{:Na}_2\text{O}$ for commercially available sodium silicates can vary from about 3.22 to about 2.0. The weight ratio of potassium silicate $\text{SiO}_2\text{:K}_2\text{O}$ can vary from about 1.65 to about 2.50. The metal silicates are available as an aqueous solution or a dry powder version. The preferred metal silicate is a sodium silicate solution with a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 3.22:1.

[0050] In the present invention a polysaccharide or derivitized polysaccharide is modified by at least one metal silicate. The modified polysaccharide or derivitized polysaccharide modified with the at least one metal silicate is then added to a papermaking process.

[0051] In one embodiment of the invention the polysaccharide or polysaccharide derivative is a cationic or amphoteric starch. The metal silicate can be added to the cationic or amphoteric starch after the starch has been cooked, while the starch is still warm ($> 65^\circ \text{C}$), has moderately cooled (30 to 65°C) or has been cooled to ambient temperatures ($< 30^\circ \text{C}$). The addition of the metal silicate to the cooked starch results in slight increases in the turbidity and viscosity of the starch solution.

[0052] The metal silicate can also be added to the aqueous starch slurry before the starch has been cooked such that the starch granules are gelatinized in the presence of the metal silicate. In this embodiment the starch is then cooked in the presence of the metal silicate. This process also produces a starch solution which is more turbid, but less viscous, than a starch solution cooked without the addition of metal silicate.

[0053] The starch modified with metal silicate may be added to the thick stock, in the machine chest or blend chest. Alternatively the starch modified with metal silicate may be added to the thin stock, after or before any of the typical thin stock addition points, i.e. fan pump, cleaners, or screen.

[0054] In the present invention, the metal silicate may be added to all of the starch, or may treat a side stream of the starch to modify a fraction of the starch. In a preferred embodiment the metal silicate is added to all of the starch. The starch modified with metal silicate may also be added simultaneously, before, or after any of the conventional wet-end additives, untreated starch, coagulants, flocculants, sizing agents, drainage aids, fillers, and the like.

[0055] The present invention will now be further described with reference to a number of specific examples that are to be regarded solely as illustrative and not restricting the scope of the present invention.

EXAMPLES

[0056] To evaluate the performance of the inventive process, a series of drainage tests were conducted utilizing a vacuum drainage test (VDT). The results of this testing demonstrate the ability of starch modified with a metal silicate to improve the drainage of the system. The device setup is similar to the Buchner funnel test as described in various filtration reference books, for example see Perry's Chemical Engineers' Handbook, 7th edition, (McGraw-Hill, New York, 1999) pp.18-78. The VDT consists of a 300-ml magnetic Gelman filter funnel, a 250-ml graduated cylinder, a quick disconnect, a water trap, and a vacuum pump with a vacuum gauge and regulator. The VDT test was

conducted by first setting the vacuum to 10 inches Hg, and placing the funnel properly on the cylinder. Next, 250 g of 0.5 wt. % paper stock was charged into a beaker and then the required additives according to treatment program (e.g., starch, alum, flocculants and drainage aids) were added to the stock under the agitation provided by an overhead mixer. The stock was then poured into the filter funnel and the vacuum pump was turned on while simultaneously starting a stopwatch. The drainage efficacy is reported as the time required to obtain 230 ml of filtrate.

[0057] Lower quantitative drainage time values represent higher levels of drainage or dewatering, which is the desired response. The values reported are the average values of two runs.

[0058] The Britt jar retention test (Paper Research Materials, Inc., Gig Harbor, WA) is known in the art. In the Britt jar retention test a specific volume of furnish was mixed under dynamic conditions and an aliquot of the furnish was drained through the bottom screen of the jar, so that the level of fine materials which were retained can be quantified. The Britt jar utilized for the present tests was equipped with 3 vanes on the cylinder walls to induce turbulent mix, and a 76 μ m screen in the bottom plate.

[0059] The Britt jar retention tests were conducted with 500 ml of the synthetic furnish, having a total solids concentration of 0.5 %. The test was conducted at 1,200 rpm with the sequential addition of starch, followed by alum, followed by polymer flocculant, followed by drainage aid; the materials were all mixed for specified interval times. After the drainage aid had been introduced and mixed, the filtrate was collected.

[0060] The retention values calculated are fines retention where the total fines content in the furnish is first determined by washing 500 ml of furnish with 10 liters of water under mixing conditions to remove all the fine particles, defined as particles smaller than the Britt jar 76 μ m screen. The fines retention for each treatment was then determined by draining 100 ml of filtrate after the described addition sequence, then filtering the filtrate through a pre-weighed

1.5 μm filter paper. The fines retention are calculated according to the following equation:

$$\% \text{ Fines retention} = (\text{filtrate wt.} - \text{fines wt.}) / \text{filtrate wt.}$$

wherein the filtrate and fines weight are both normalized to 100 ml. The retention values obtained represent the average of 2 replicate runs.

[0061] The furnish employed in the series of tests was a synthetic alkaline furnish. This furnish was prepared from hardwood and softwood dried market lap pulps, and from water and further materials. First the hardwood and softwood dried market lap pulp were separately refined in a laboratory Valley Beater (Voith, Appleton, Wis.). These pulps were then added to an aqueous medium. The aqueous medium utilized in preparing the furnish comprises a local tap water, and was further modified with inorganic salts added in amounts so as to provide this medium with a m-alkalinity of 75-100 ppm as NaHCO_3 and a total solution conductivity of 750 – 1000 $\mu\text{S/cm}$. To prepare the furnish, the hardwood and softwood were dispersed into the aqueous medium at weight ratios of about 67% hardwood and 33% softwood. Precipitated calcium carbonate (Albacar® 5970, Minerals Technologies, Bethlehem, PA) was introduced into the furnish at 25 weight percent, based on the combined dry weight of the pulps, so as to provide a final furnish comprising 80% fiber and 20% PCC filler. The furnish had a consistency of 0.5% (total solids of 0.5 lbs per 100 lbs of water).

[0062] The modified starch utilized in the present system is presented in Table 1. Stalok® 400 is a cationic potato starch (A. E. Staley, Decatur, Ill.). The metal silicate is Silicate O, a liquid sodium silicate possessing a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.22:1 (PQ Corporation, Valley Forge, PA); the dosage of metal silicate in all examples is based upon active SiO_2 . The alum is aluminum sulfate-octadecahydrate available as a 50% solution (Delta Chemical Corporation, Baltimore, Md.). Perform® PC 8138 is a cationic emulsion flocculant (Hercules Incorporated, Wilmington, DE). Perform® SP 7200 is an advanced structured organic microparticulate (Hercules Incorporated, Wilmington, DE).

[0063] A 2% starch solution was prepared by heating adding 4 grams Stalok® 400 cationic starch to 196 grams deionized water and heating the starch to 95° C for 30 minutes until a clear, viscous solution was produced. The starch solution was allowed to cool to ambient temperatures.

[0064] A blend of cationic starch and sodium silicate at the indicated ratio was prepared by adding the indicated amount of metal silicate to the cooked starch solution. For example, a 10:1 starch:metal silicate solution was prepared by adding 0.68 grams of Silicate O (29% active sodium silicate) to 100 grams of 2% starch cooked starch solution.

[0065] A solution was also prepared by cooking the starch in the presence of the metal silicate. In this example, a 10:1 cooked solution was prepared by mixing 1.38 grams of Silicate O (29% active sodium silicate) with 198.62 grams of deionized water. 4 grams of Stalok® 400 cationic starch was added and the solution was heated to 95° C for 30 minutes until a turbid, viscous solution was produced. The starch solution was allowed to cool to ambient temperatures.

[0066] The data in Table 1 illustrate the improved retention and drainage performance of the invention, where starch modified with a metal silicate provides better drainage compared to the unmodified starch. The data further illustrate the metal silicate can be blended with the starch after cooking, or added to the starch slurry prior to cooking.

[0067]

TABLE 1

Starch	Starch Dose*, #/T	Metal Silicate	Ratio Starch: Metal Silicate	Metal Silicate Dose*, #/T	Drain Time, seconds	Fines Retention, %	Comments
Stalok 400	10	None		0	19.1	82.8	
Stalok 400	10	Silicate O	10:1	1	16.5		cooked together
Stalok 400	10	Silicate O	10:1	1	15.4	89.3	Blend
Stalok 400	10	Silicate O	2:1	5	15.8		cooked together
Stalok 400	10	Silicate O	2:1	5	15.9		Blend

Starch was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual quantities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding starch dose and metal silicate dose. The Metal Silicate Dose is measured as Active metal silicate.

[0068] The addition sequence is as follows, with 10 seconds mix time between each additive:

Starch or modified starch;

Alum at a dosage level of 5 lb./ton;

Perform PC 8138 at a dosage level of 0.4 lb./ton;

Perform SP 7200 at a dosage level of 0.4 lb./ton.

[0069] A series of drainage tests was conducted with the starch blended with the metal silicate at the indicated ratio utilizing the VDT, and the data are presented in Table 2. The materials, methods, and addition sequence are as specified in Table 1. The data in Table 1 illustrate the improved drainage of the

inventive process compared to a starch that is not modified with metal silicate. Improved drainage is noted with higher levels of metal silicate.

TABLE 2

Starch	Starch Dose*, #/T	Metal Silicate	Ratio Starch: Metal Silicate	Metal Silicate Dose*, #/T	Drain Time, seconds
Stalok 400	10	None		0	21.6
Stalok 400	10	Silicate O	20:1	0.5	18.1
Stalok 400	10	Silicate O	10:1	1	15.9
Stalok 400	10	Silicate O	5:1	2	14.4

Starch was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual quantities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding starch dose and metal silicate dose. The Metal Silicate Dose is measured as Active metal silicate.

[0070] A series of drainage tests was conducted with the starch blended with the metal silicate at the indicated ratio using the VDT, and the data are presented in Table 3. Cato® 232 is a cationic waxy maize starch (National Starch, Bridgewater, NJ). Stalok® 300 is a cationic corn starch (A. E. Staley, Decatur, Ill.). The materials, methods, and addition sequence are as specified in Table 1. The data in Table 3 illustrate the drainage improvement provided with the inventive process compared to an unmodified starch, using example of waxy maize and corn starch.

TABLE 3

Starch	Starch Dose*, #/T	Metal Silicate	Ratio Starch: Metal Silicate	Metal Silicate Dose*, #/T	Drain Time, seconds
Cato 232	10	None		0	20.4
Cato 232	10	Silicate O	20:1	0.5	16.9
Cato 232	10	Silicate O	10:1	1	15.7
Cato 232	10	Silicate O	5:1	2	13.7
Stalok 300	10	None		0	19.2
Stalok 300	10	Silicate O	20:1	0.5	17.3
Stalok 300	10	Silicate O	10:1	1	17.0
Stalok 300	10	Silicate O	5:1	2	13.7

Starch was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual qualities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding starch dose and metal silicate dose.

[0071] A series of drainage tests was conducted with the VDT with the starch blended with the metal silicate at the indicated ratio; the data are presented in Table 4. Silicate O is sodium silicate possessing a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 3.22:1, Silicate M is sodium silicate possessing a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 2.58:1, and Silicate D is sodium silicate possessing a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio of 2.00:1 (PQ Corporation, Valley Forge, PA). The materials, methods, and addition sequence are as specified in Table 1, with the exception of the Perform® SP 7200 dosage as indicated. The data in Table 4 illustrate the improved drainage provided by the inventive process compared to an unmodified starch. Good drainage activity is provided with sodium silicates possessing various ratios of $\text{SiO}_2\text{:Na}_2\text{O}$.

TABLE 4

Starch	Starch Dose*, #/T	Starch Cook Concentration	Metal Silicate	Ratio Starch: Metal Silicate	Dose*, #/T	SP 7200 Dose, #/T	Drain Time, seconds
Stalok 400	10	4	None		0	0.4	20.5
Stalok 400	10	4	Silicate D	2.5:1	4	0.4	19
Stalok 400	10	4	Silicate O	2.5:1	4	0.4	15.6
Stalok 400	10	3	Silicate M	4:1	2.5	0.4	14.2
Stalok 400	10	4	Silicate D	10:1	1	0.4	17.6
Stalok 400	10	2	Silicate D	2.5:1	4	0.4	19.4
Stalok 400	10	2	Silicate O	2.5:1	4	0.4	16.1
Stalok 400	10	2	Silicate D	10:1	1	0.4	18.7
Stalok 400	10	4	Silicate O	10:1	1	0.4	15.8
Stalok 400	10	2	Silicate O	10:1	1	0.4	15.1

Starch was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual qualities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding starch dose and metal silicate dose.

[0072] Another series of drainage tests was conducted with the VDT with the starch blended with the metal silicate at the indicated ratio utilizing starches with different degrees of substitution; the data are presented in Table 5. Stalok® 430 is a cationic corn starch with a degree of substitution of 0.18; Stalok® 400 is a cationic potato starch with a DS = 0.28; and Stalok® 410 is a cationic potato starch with a DS = 0.35. (A. E. Staley, Decatur, Ill.) The materials, methods, and addition sequence are as specified in Table 1. The data in Table 5 illustrate the improved drainage provided by the inventive process compared to an unmodified starch, utilizing starches with varying degrees of substitution.

TABLE 5

Starch	Starch Degree of Substitution (DS)	Starch Dose*, #/T	Metal Silicate	Ratio Starch: Metal Silicate	Metal Silicate Dose*, #/T	Drain Time, seconds
Stalok 430	0.18	10	None		0	17.3
Stalok 430	0.18	10	Silicate O	10:1	1	16.8
Stalok 400	0.28	10	None		0	19.8
Stalok 400	0.28	10	Silicate O	10:1	1	15.6
Stalok 410	0.35	10	None		0	21.4
Stalok 410	0.35	10	Silicate O	10:1	1.0	15.5

Starch was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual quantities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding starch dose and metal silicate dose.

[0073] Another series of drainage tests was conducted with the VDT utilizing a cationic guar as the polysaccharide, which was blended with the metal silicate at the indicated ratio; the data are presented in Table 6. N-Hance 3196 is a cationically modified guar gum (Ashland Aqualon, Wilmington, DE) The materials, methods, and addition sequence are as specified in Table 1. The data in Table 6 illustrate the improved drainage provided by the inventive process compared to an unmodified cationic guar.

TABLE 6

Polysaccharide (PS)	PS Dose*, #/T	Metal Silicate	Ratio PS: Metal Silicate	Metal Silicate Dose*, #/T	Drain Time, seconds
N-Hance	10	None		0	39.2
N-Hance	10	Silicate O	10:1	1	26.4

The polysaccharide was modified with metal silicate prior to addition to the pulp slurry. Dose # indicates individual quantities of starch and metal silicate prior to modification and subsequent addition to the pulp slurry. Total #/T of modified starch including metal silicate is found by adding polysaccharide dose and metal silicate dose.

[0074] While the present invention has been described with respect to particular embodiment thereof, it is apparent that numerous other forms and modifications will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications, which are within the true scope of the invention.

CLAIMS:

1. A papermaking process comprising adding to a papermaking slurry, at least one polysaccharide or polysaccharide derivative, wherein the polysaccharide or polysaccharide derivative has been modified with at least one metal silicate, wherein the at least one polysaccharide or polysaccharide derivative is selected from the group consisting of derivatized polysaccharides containing a cationic nitrogen group, a blend of cationic and anionic polysaccharides or combinations thereof.
2. The method of claim 1 wherein the at least one polysaccharide or polysaccharide derivative comprises a least one starch.
3. The method of claim 2 where the starch is selected from the group consisting of a potato starch; corn starch; wheat starch; tapioca starch; rice starch; derivatives thereof and combinations thereof.
4. The method of claim 1 where the at least one metal silicate is selected from the group consisting of sodium silicate, potassium silicate, sodium metasilicate or combinations thereof
5. The method of claim 4 wherein the metal silicate is sodium silicate.
6. The method of claim 1 wherein the ratio of polysaccharide to metal silicate is from 1:10 to 100:1.
7. The method of claim 6 where the ratio of polysaccharide to metal silicate is from 1:1 to 50:1.
8. A papermaking process comprising adding to a papermaking slurry, at least one starch or starch derivative, wherein the starch or starch derivative has been modified with a metal silicate, wherein the at least one starch or starch derivative is selected from the groups consisting of derivatized starch containing a cationic nitrogen group or a blend of cationic and anionic starches.

9. The method of claim 7 where the starch is selected from the group consisting of potato starch; corn starch; wheat starch; tapioca starch; rice starch; derivatives thereof and combinations thereof.

10. The method of claim 7 wherein the metal silicate is selected from the group consisting of sodium silicate, potassium silicate, sodium metasilicate and combinations thereof.

11. The method of claim 7 wherein the ratio of starch to metal silicate is from 1:10 to 100:1.

12. The method of claim 11 wherein the ratio of starch to metal silicate is from 1:1 to 50:1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/000538

A. CLASSIFICATION OF SUBJECT MATTER

INV. D21H17/13 D21H17/24 D21H17/28 D21H17/29 D21H21/10
D21H17/68 D21H17/69 D06M13/513

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched. (classification system followed by classification symbols)
D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 89/12661 A (DELTA CHEMICALS INC [US]) 28 December 1989 (1989-12-28) page 2, line 21 - page 3, line 10 page 4, line 4 - page 5, line 32 page 7, line 2 - line 11; claims; examples	1-3,6-9, 11,12
X	US 5 185 206 A (RUSHMERE JOHN D [US]) 9 February 1993 (1993-02-09) cited in the application column 1, line 35 - line 48 column 5, line 12 - line 26 column 13, line 66 - column 15, line 55; claims	1-3,8,9
X	WO 93/15271 A (KEMIRA KEMI AB [SE]) 5 August 1993 (1993-08-05) page 4, line 11 - line 17 page 5, line 28 - page 6, line 8; claims 1,10	1,2,4,5, 8,10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 8912661	A	28-12-1989	AU 632758 B2	14-01-1993
			AU 3859589 A	12-01-1990
			BR 8907511 A	28-05-1991
			CA 1329312 C	10-05-1994
			DE 68912346 D1	24-02-1994
			DE 68912346 T2	01-09-1994
			EP 0446205 A1	18-09-1991
			JP 3505899 T	19-12-1991
			US 5071512 A	10-12-1991
US 5185206	A	09-02-1993	NONE	
WO 9315271	A	05-08-1993	FI 943549 A	28-09-1994
			NO 942808 A	28-09-1994
			US 5670021 A	23-09-1997