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(54) **PAPERMAKING AND PRODUCTS MADE THEREBY WITH HIGH SOLIDS GLYOXALATED-POLYACRYLAMIDE AND SILICON-CONTAINING MICROPARTICLE**

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(57) **ABSTRACT**

Enhancement of papermaking drainage and retention properties of aqueous cellulosic suspensions used for production of paper or paper board with a retention/drainage additive system including high solids glyoxalated polyacrylamide polymers in combination with silicon-containing microparticles is described.

**PAPERMAKING AND PRODUCTS MADE  
THEREBY WITH HIGH SOLIDS  
GLYOXALATED-POLYACRYLAMIDE AND  
SILICON-CONTAINING MICROPARTICLE**

**[0001]** This application claims the benefit under 35 U.S.C. §119(e) of prior U.S. Provisional Patent Application No. 61/221,107, filed Jun. 29, 2009, which is incorporated in its entirety by reference herein.

**BACKGROUND OF THE INVENTION**

**[0002]** The present invention relates to papermaking, and more particularly, to papermaking and products made thereby with high solids glyoxalated polyacrylamide and silicon-containing microparticles.

**[0003]** In the production of paper and paperboard from a dilute aqueous suspension of cellulose fibers on papermaking apparatus, the suspension can be passed through one or more shear stages and the resultant suspension is drained through a wire to form a sheet, which is then dried. Process improvements have been sought in the past, for example, in retention, drainage, and drying, and in the formation (or structure) properties of the final paper sheet. Retention is a term used in papermaking to indicate the extent to which the pulp fibers and other additives which are added to the furnish are retained in the finished paper. A retention aid generally acts by increasing the flocculating tendency of the pulp fibers and additives to inhibit their loss during drainage through the paper machine wires or screens. Drainage or de-watering is another papermaking requirement.

**[0004]** U.S. Pat. No. 3,556,932 relates to glyoxalated polyacrylamide that can be prepared by reacting glyoxal with a cationic polyacrylamide under slightly alkaline conditions and its application to increase paper wet strength. Sodium bisulfite is used as an anti-gelation agent. The cationic polyacrylamide (base polymer) has a molecular weight of 7000-25,000 Daltons. The cationic charge is obtained by copolymerizing acrylamide with a cationic monomer, which is typically dimethyldiallylammonium chloride. The base polymer is exemplified in U.S. Pat. No. 3,556,932 as having a molecular weight below 25,000 Daltons and an acrylamide: DADMAC molar ratio of 99:1 to 75:25.

**[0005]** WO 2006/068964 relates to a reactive cationic resin for use as dry and wet strength agents in sulfite ion-containing papermaking systems. The cationic resin includes a dialdehyde reactive copolymer wherein the cationic co-monomer has greater than 10 mole % of the dialdehyde reactive copolymer before reaction with dialdehyde. WO 2006/068964 also relates to a process for making paper in which the above cationic resin was added to an aqueous pulp suspension containing a sulfite level in excess of 20 ppm.

**[0006]** WO 2008/157321 relates to storage-stable glyoxalated polyacrylamide polymers and high solids aqueous compositions formulated with them, which can be used as additives for papermaking, providing paper with good dry and temporary wet strength, and increasing papermaking de-watering rates.

**[0007]** U.S. Pat. No. 4,961,825 relates to production of paper or pulp sheets from a paper stock with a binder added which comprises cationic and anionic components. The anionic component consists of colloidal anionic particles having at least one surface layer of aluminum silicate or aluminum-modified silicic acid, such that the surface groups

of the particles contain silicon and aluminum atoms in a ratio of from 9.5:0.5 to 7.5:2.2, and the cationic component consists of cationic carbohydrate having a degree of substitution of 0.01-1.0.

**[0008]** U.S. Pat. No. 5,368,833 relates to silica sols having a high content of microgel and aluminum modified particles with high specific area. The sols are said to be suitable for use as additives, in combination with cationic polymers, in papermaking.

**[0009]** U.S. Pat. No. 5,603,805 relates to silica sols with a high content of microgel and particles with a specific surface area within a range of 300 to 700 m<sup>2</sup>/g. The sols are said to be suitable for use as additives in papermaking in combination with cationic polymers such as cationic acrylamide based polymers.

**[0010]** U.S. Pat. No. 4,305,781 relates to methods of making newsprint, Kraft or fluting medium from an aqueous suspension of cellulosic fibers, where drainage and retention properties of the suspension are said to be improved by including a water soluble high molecular weight substantially non-ionic polymer and a bentonite-type clay.

**[0011]** U.S. Pat. No. 4,753,710 relates to a process in which paper or paper board is made by passing an aqueous cellulosic substrate through a centriscreeen or other shear device and then draining the purified suspension, and an improved combination of retention, drainage, drying and formation is said to be achieved by adding to the suspension an excess of high molecular weight linear synthetic cationic polymer before shearing the suspension and adding bentonite after shearing.

**[0012]** U.S. Pat. No. 4,388,150 relates to a papermaking process in which an aqueous papermaking stock or white water has added a binder comprising colloidal silicic acid and cationic starch.

**SUMMARY OF THE PRESENT INVENTION**

**[0013]** A feature of the present invention is to provide an enhanced additive system for improving wet-end drainage and retention in papermaking using glyoxalated polyacrylamide ("G-PAM") polymers and microparticles.

**[0014]** Another feature of the present invention is to provide increased papermaking retention efficiencies and de-watering rates with a retention/drainage additive system comprising high solids glyoxalated polyacrylamide polymer and silicon-containing microparticles.

**[0015]** An additional feature of the present invention is to provide decreased filtrate turbidities and more rapid drainage rates with an additive system comprising a high solids glyoxalated polyacrylamide polymer and silicon-containing microparticles.

**[0016]** Another feature of the present invention is to provide lowered filtrate turbidities and comparable drainage rates as polyamine coagulant products with an additive system comprising a high solids glyoxalated polyacrylamide polymer and silicon-containing microparticles.

**[0017]** A further feature of the present invention is to provide paper products containing a glyoxalated polyacrylamide polymer and silicon-containing microparticles.

**[0018]** An additional feature of the present invention is to provide a process for papermaking which can improve the retention/drainage properties, as well as provide improvements in dry strength impact.

**[0019]** Additional features and advantages of the present invention will be set forth in part in the description that follows, and in part will be apparent from the description, or

can be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

**[0020]** To achieve these and other advantages, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates, in part, to a process for making paper, and the products thereof, comprising adding silicon-containing microparticles and a glyoxalated polyacrylamide polymer containing at least about 25% by weight cationic monomer to an aqueous suspension containing cellulosic fibers, and forming said suspension into a water-laid web and drying said web to form paper. The silicon-containing microparticles are added, in combination with the glyoxalated polyacrylamide polymer, in an amount effective to increase fiber retention and dewatering rate as compared to paper made with the suspension absent the silicon-containing microparticles. The glyoxalated polyacrylamide polymer component of the additive system can be introduced, for example, as a high solids aqueous composition thereof having a high active polymer concentration, for example, about 10% by weight or more of the glyoxalated polyacrylamide polymer. The combination of silicon-containing microparticles with high solids glyoxalated polyacrylamide polymer in the wet-end of a papermaking process can greatly improve retention and drainage performance, and/or dry strength impact.

**[0021]** The silicon-containing microparticles can comprise solid microparticles containing silicon (Si). The solid microparticles containing silicon can be, for example, inorganic crystalline and/or non-crystalline (e.g., amorphous) materials. The microparticles can be used, for example, in dry powder form or dispersed form (e.g., suspensions, slurries, colloids, sols). The silicon-containing microparticles are selected, for example, from microparticles of silica, bentonite, or a combination thereof. The silicon-containing microparticles can comprise, for example, amorphous silica microparticles. The silicon-containing microparticles can comprise, for example, colloidal silica comprising a surface area from 300 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g, 500 m<sup>2</sup>/g to 800 m<sup>2</sup>/g, or 600 m<sup>2</sup>/g to 750 m<sup>2</sup>/g, and/or an S-value from 80% to 20%, 70% to 30%, or 60% to 40%. The colloidal silica can optionally be surface modified, such as aluminate-treated, metal-treated, or untreated. The silicon-containing microparticles can comprise, for example, bentonite microparticles. The bentonite optionally can be chemically modified or untreated. The silicon-containing microparticles can have an average particle size, for example, of not greater than about 1,000 nm, 1 nm to 750 nm, 2 nm to 500 nm, 3 nm to 500 nm, 4 nm to 100 nm, 5 nm to 50 nm, or 10 nm to 30 nm. The silicon-containing microparticles can have an absolute particle size within one or more of these size ranges. The dry particle size distribution of the silicon-containing particles can be, for example, such that at least 90%, or at least 95%, or at least 99% up to 100%, have an absolute particle size of less than 1000 nm, or less than 750 nm, or less than 500 nm, or less than 100 nm, or less than 75 nm, or less than 50 nm. The paper made in processes according to the present invention can comprise from about 0.05 to about 2.5 pounds (lb.) silicon-containing microparticles/ton dry fiber, about 0.1 to about 1 lb. silicon-containing microparticles/ton dry fiber, or about 0.2 to about 0.8 lb. silicon-containing microparticles/ton dry fiber.

**[0022]** The glyoxalated polyacrylamide polymer can comprise a reaction product between glyoxal and a cationic polyacrylamide base polymer, wherein the cationic polyacrylamide base polymer can comprise from about 75% to about 10%, by weight, acrylamide monomer and from about 25% to about 90%, by weight, cationic monomer copolymerizable with the acrylamide monomer, and has sufficient glyoxal-reactive amide substituents and —CHOHCHO substituents to be thermosetting. The concentration of the glyoxalated acrylamide polymer in an aqueous carrier can be from about 10% to about 30%, by weight, or, from about 11% to about 15%, by weight, or, from about 12% to about 15%, by weight, glyoxalated acrylamide polymer (on an active solids basis). The paper made in processes according to the present invention can have the glyoxalated polyacrylamide polymer added in an amount of from about 0.5 to about 12 pounds (lb.) polymer/ton dry fiber, about 1 to about 11 lb. polymer/ton dry fiber, or about 3 to about 10 lb. polymer/ton dry fiber.

**[0023]** The glyoxalated acrylamide polymer can comprise, for example, from about 70% to about 30%, by weight, acrylamide monomer and from about 30% to about 70%, by weight, cationic monomer, or, for example, from about 65% to about 50%, by weight, acrylamide monomer and from about 35% to about 50%, by weight, cationic monomer, or, for example, from about 62% to about 55%, by weight, acrylamide monomer and from about 38% to about 45%, by weight, cationic monomer, and can have sufficient glyoxal-reactive amide substituents and —CHOHCHO substituents to be thermosetting. The cationic monomer of the polymer can be 2-vinylpyridine, 2-vinyl-N-methylpyridinium chloride, (p-vinylphenyl) trimethyl ammonium chloride, diallyldimethylammonium chloride, 2-(dimethylamino)ethyl acrylate, trimethyl(p-vinylbenzyl)ammonium chloride, p-dimethylaminoethylstyrene, dimethylaminopropyl acrylamide, 2-methylacryloxyethyltrimethyl ammonium methylsulfate, or 3-acrylamido-3-methylbutyl trimethyl ammonium chloride, or any combination thereof. The cationic monomer can be diallyldimethyl ammonium chloride. The acrylamide monomer can be replaced by other primary amide-containing monomers such as methacrylamide, ethylacrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, or N-ethyl methacrylamide, or any combination thereof. The acrylamide monomer can be acrylamide. The glyoxalated polyacrylamide polymer can be the reaction product of glyoxal and a base polymer comprising the acrylamide monomer and the cationic monomer in a weight ratio, ranging, for example, from about 0.01 to about 0.6:1, and, for example, from about 0.10 to about 0.30:1. The base polymer can have a molecular weight (weight average molecular weight) ranging, for example, from about 500 Daltons to 100,000 Daltons, for example, 3,000 to 20,000 Daltons, for example, from about 3,000 Daltons to about 13,000 Daltons, or, for example, 5,000 Daltons to 9,000 Daltons.

**[0024]** As part of the present invention, a paper product is provided comprising the high solids, higher charged glyoxalated polyacrylamide polymer and silicon-containing microparticles of the additive systems of the present invention. Paper products made with the improved retention/drainage additive system according to the present invention have useful dry and temporary wet strength performances, and other mechanical properties typically desired of paper products. The paper product can comprise, for example, a cellulosic fibrous non-woven web. A paper product can comprise a paper layer containing the glyoxalated polyacrylamide poly-

mer and silicon-containing microparticles, wherein the product is, for example, paper sheeting, paperboard, tissue paper, or wall board. Paper products include, for example, all grades of paper, newsprint, linerboard, fluting medium, and Kraft, and other paper materials.

**[0025]** It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention, as claimed.

#### DETAILED DESCRIPTION OF THE PRESENT INVENTION

**[0026]** The present invention relates, in part, to combinations of glyoxalated polyacrylamide polymers and silicon-containing microparticles as co-additives in papermaking to provide paper products made with improved drainage and retention. A process is provided for making paper comprising adding silicon-containing microparticles and a glyoxalated polyacrylamide polymer containing at least about 25% by weight cationic monomer to an aqueous suspension containing cellulosic fibers, and forming said suspension into a water-laid web and drying said web to form paper. Paper products of the process are also provided. The suspension can comprise, consist essentially of, or consist of silicon-containing microparticles, a glyoxalated polyacrylamide polymer, and cellulosic fibers.

**[0027]** Many retention/drainage aids decrease paper dry strength or have no dry strength impact in papermaking. However, with the present invention, an increase in dry strength is achievable and, in addition, the retention/drainage can be improved. The dry strength and/or retention/drainage can increase 10% or more, 20% or more, 30% or more, as compared to the same composition but without a microparticle present with the base polymer (e.g., G-PAM).

**[0028]** The use of silicon-containing particle as solid microparticles in combination with the high solids glyoxalated polyacrylamide polymers in a wet-end of papermaking, instead of larger silicon-containing particles can be important to achieving the unique retention and drainage performance. The additional presence of the silicon-containing microparticles with the high solids glyoxalated polyacrylamide polymers in a papermaking process according to the present invention has been found to preferably have a synergistic effect, wherein the retention/drainage performance is increased and/or the dry strength beyond what is obtained with the same glyoxalated polyacrylamide polymers alone. Further, the combined use of high solids glyoxalated polyacrylamide polymers and silicon-containing microparticles can provide reduced filtrate turbidities and/or faster drainage rates than some commercial glyoxalated polyacrylamide products when used as commercially supplied or in combination with similar silicon-containing microparticles for sake of comparison. The preferred joint improvement in fiber retention and drainage rate properties obtained in paper products made with G-PAM/silicon-containing microparticle additive systems according to the present invention is unexpected and surprising. In addition, the combined use of high solids glyoxalated polyacrylamide polymers and silicon-containing microparticles according to the present invention can provide both reduced filtrate turbidities and at least comparable drainage rates than some commercial polyamine coagulant products when used as commercially supplied or in combination with similar silicon-containing microparticles for sake of comparison. The ability to both increase drainage

rates and improve retention efficiencies allows for more economical production to be obtained, as, for example, production cycles can be accelerated without increasing white water recycling or handling/disposal requirements. Further, the combinations of glyoxalated polyacrylamide polymers and silicon-containing microparticles according to the present invention also can be applied to reduce other additive requirements of the papermaking process. For example, the high solids G-PAM compositions of the combination can multi-task to replace both conventional G-PAM products used as dry strength resin and also conventional polyamine products used as coagulant.

**[0029]** The process according to the present invention can be practiced on conventional papermaking machines, such as a Fourdrinier type paper machine, with modifications that can be made in view of the present invention. The glyoxalated polyacrylamide polymers and silicon-containing microparticles can be added at the wet-end of a paper-making facility to the dilute cellulose fiber suspensions for the enhancement of water removal and retention of fine particles during papermaking. The glyoxalated polyacrylamide polymers and silicon-containing microparticles components can be added to the papermaking machine as a pre-mixture with each other, or separately in any order of addition. The components can be added as separate batches, as combined batches, sequentially, continuously, semi-continuously, or periodically. The G-PAM polymer(s) can be added in liquid form and can be added separate from the microparticles. The microparticles can be added as a suspension. The microparticles or suspension thereof can be added separately. Any references to a retention/drainage additive system herein with regard to these two components refer to their joint presence after addition in any manner or sequence to the fiber suspension to be treated. Both components can be introduced to the fiber suspension before sheet formation. This can be carried out, for example, by adding the glyoxalated polyacrylamide polymers in the form of an aqueous composition, and the silicon-containing microparticles in dry powder form or as an aqueous dispersion (same or different as the G-PAM polymer composition), to the fiber suspension in a mixing tank or some other point in the papermaking machine in which there is suitable agitation, such that the two components are dispersed with the components forming the paper and thus can act simultaneously with each other and/or with the components for forming the paper. Pulp collected on a forming wire screen can be further drained, pressed, and dried, and optionally further can be coated and converted. Any pulp fibers drained through the wire can be optionally recirculated to a white water silo.

**[0030]** Before de-watering, the fiber suspension treated with the combination of glyoxalated polyacrylamide polymers and silicon-containing microparticles can have one or more optional additional additives mixed into the fiber suspension, such as one or more process additives and/or functional additives, including those conventionally used in papermaking. For example, optional additives can be introduced, for example, in a conventional blend chest or other convenient location within a papermaking system before or after sheet formation. These optional additives can include, e.g., additional polymers such as cationic, anionic and/or non-ionic polymers, clays, other fillers, dyes, pigments, defoamers, pH adjusting agents such as alum, sodium aluminate, and/or inorganic acids, such as sulfuric acid, microbicides, cationic colloidal alumina microparticles, coagulants, flocculants, and/or other conventional and non-conventional

papermaking or processing additives. These optional additives, if used, are used in an amount effective for their respective purpose. In this respect, it is important to ensure that the content of these other optional agents do not adversely effect or impede the beneficial drainage and retention effects imparted by the glyoxalated polyacrylamide polymers and silicon-containing microparticles. The additive system comprising the glyoxalated polyacrylamide polymer composition and silicon-containing microparticles can be added to fiber suspension over a wide range of pH values. However, best results should be obtained by adding the composition to the fiber suspension at a pH of from about 4 to about 8, most preferably from 5.5 to 7.0. The G-PAM compositions and silicon-containing microparticles described herein are readily absorbed or retained by the cellulose fibers at these pH values.

**[0031]** As indicated, silicon-containing microparticles are one of the components of the improved retention/drainage additive system of the present invention. The silicon-containing microparticles are, for example, solid microparticles containing silicon (Si). The solid microparticles containing silicon can be, for example, inorganic crystalline or non-crystalline materials. The silicon content of the microparticles can be, for example, chemically bonded (e.g., covalent, ionic, metallic), complexed, hydrogen bonded, van der Waals force bonded, and/or physically entrapped, or combinations thereof. The microparticles can be added to the fiber suspensions being treated as dry powders or as dispersions in water or other suitable liquid carriers. Use of microparticle dispersions can assist in distribution of the solid microparticles in the fiber suspensions and/or can avoid possible practical concerns associated with handling and use of dry powders.

**[0032]** The silicon-containing microparticle can comprise silica microparticles. The silica microparticles can be used in dry powder form (including dry to the touch gels) or in dispersed form. The silica microparticles can comprise, for example, amorphous silica microparticles or crystalline silica microparticles. The silica microparticles can be, for example, in the form of colloidal silica, colloidal silicic acid, silica sols, fumed silica, agglomerated silicic acid, silica gels, and precipitated silicas, or any combinations thereof. For instance, silica (e.g., amorphous silica nanoparticles and bentonite) can be added separately or as a mixture (e.g., as a suspension). The silica microparticles can be, for example, inorganic silicates, such as aluminum silicates (e.g., kaolin clay). The silica microparticles can be dispersed amorphous silica microparticles. For purposes herein, the terminology "silica microparticles" means finely divided silica having a particle size according to the present invention, and the term encompasses silica primary particles, silica aggregates (i.e., unitary clusters of a plurality of silica primary particles), silica agglomerates (i.e., unitary clusters of a plurality of silica aggregates), individually or in combinations thereof.

**[0033]** The silicon-containing microparticles can comprise, for example, colloidal silica comprising a surface area from 300 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g, 500 m<sup>2</sup>/g to 800 m<sup>2</sup>/g, or 600 m<sup>2</sup>/g to 750 m<sup>2</sup>/g, and an S-value from 80% to 20%, 70% to 30%, or 60% to 40%. For purposes herein, the "surface area" and "S-value" of the silica particles can be determined by respective methods such as described in U.S. Pat. No. 5,603,805, which is incorporated in its entirety by reference herein. The colloidal silica can be aluminate-treated or untreated. The silica microparticles have a dry particle size, for example,

of not greater than about 1,000 nm, 1 nm to 750 nm, 2 nm to 500 nm, 3 nm to 500 nm, 4 nm to 100 nm, 5 nm to 50 nm, or 10 nm to 30 nm, on an average or absolute particle size basis. The silica microparticles can have an absolute particle size within one or more of these size ranges. The dry particle size distribution of the silica particles is, for example, such that at least 90%, or at least 95%, or at least 99% up to 100%, have an absolute particle size of less than 1000 nm, or less than 750 nm, or less than 500 nm, or less than 100 nm, or less than 75 nm, or less than 50 nm. The presence of larger sized silicon-containing particles in the wet-end of papermaking is not excluded; however, they are not needed for purposes of obtaining the improved retention and drainage according to the present invention.

**[0034]** Colloidal silica solutions are frequently commercially supplied as 5% up to 50% by weight dispersions, which typically are diluted for use in processes according to the present invention, although not necessarily. A preferred commercial dispersion of silica is available from Eka Chemicals, Inc. (Marietta, Ga.), such as EKA NP series, e.g., Eka NP 890, a high-solids, surface-modified, structured, anionic silica sol for all pH ranges. As indicated, the silica dispersions may be used as received or as diluted for use according to the present invention. The concentration of silica microparticles when used in an aqueous silica suspension, colloid, sol, or other dispersion, can be, for example, between about 0.1% and about 20% by weight, or about 5 to about 15% by weight, or other ranges. The viscosity of the aqueous silica suspension can be less than 50 mPa·s (measured using a Brookfield viscometer at 100 rpm).

**[0035]** The paper made in processes according to the present invention can comprise from about 0.05 to about 2.5 pounds (lb.) silica microparticles/ton dry fiber, about 0.1 to about 1 lb. silica microparticles/ton dry fiber, or about 0.2 to about 0.8 lb. silica microparticles/ton dry fiber (on a solids/solids basis). The amount of silica microparticles added, on a solids basis, can be expressed in weight percentage terms, wherein the amount of added silica microparticles can be as low as about 0.0025 wt % of the dry weight of the cellulose fibers, but usually does not exceed about 0.125% by weight. An amount of silica microparticles in the range of about 0.005 wt % to 0.1 wt % of the dry paper weight is more usual.

**[0036]** As indicated, the silicon-containing microparticle can be bentonite microparticles. The bentonite microparticles can be used in dry powder form or in dispersed form. Bentonite generally comprises an absorbent aluminum phyllosilicate, generally impure clay consisting mostly of montmorillonite. Types of bentonites can include different dominant metals, such as potassium, sodium, calcium, and aluminum, or other metal. As regards the bentonite dispersion, this preferably can be a bentonite suspension consisting of any type of commercial product referred to as bentonite or as bentonite-type clay, i.e. anionic swelling clays such as sepiolite, attapulgite, preferably, montmorillonite. The clays may or may not be chemically modified, for example, by alkaline treatment to exchange the calcium of bentonite for an alkali metal or alkali (e.g., sodium, potassium, or ammonium). The montmorillonite clays that can be suitable include, for example, Wyoming bentonites and soapy earths. The swelling clays are usually metal silicates comprising a metal chosen from aluminum and magnesium, and optionally other metals, and the ratio of silicon atoms to metal atoms at the surface of the clay particles, and generally within their structure, is from 5/1 to 1/1. For most montmorillonites, the ratio is relatively low, the

metal being essentially or totally aluminum, but with a small amount of magnesium and occasionally with, for example, a small amount of iron. However, in other swelling clays, all or some of the aluminum is replaced with magnesium and the ratio may be very low, for example about 1.5 for sepiolite. The use of silicates in which some of the aluminum has been replaced with iron also can be used.

**[0037]** The bentonite microparticles can have a dry particle size, for example, of not greater than about 1,000 nm, 1 nm to 750 nm, 2 nm to 500 nm, 3 nm to 500 nm, 4 nm to 100 nm, 5 nm to 50 nm, or 10 nm to 30 nm, on an average or absolute particle size basis. The bentonite microparticles can have an absolute particle size within one or more of these size ranges. The dry particle size distribution of the bentonite particles is, for example, such that at least 90%, or at least 95%, or at least 99% up to 100% (% based on the total weight of microparticles), have an absolute particle size of less than 1000 nm, or less than 750 nm, or less than 500 nm, or less than 100 nm, or less than 75 nm, or less than 50 nm. The surface area of the bentonite before swelling can be at least 30 m<sup>2</sup>/g, at least 50 m<sup>2</sup>/g, or from 60 to 90 m<sup>2</sup>/g, and the surface area after swelling can be from 400 to 800 m<sup>2</sup>/g. The bentonite preferably swells, for example, by a factor of at least 15 to 20-fold. The size of at least 90% (by weight) of the particles after swelling is preferably less than 2 microns, or 1 micron, or other values. Bentonite microparticles having these properties can be produced by known methods or commercially obtained, such as by using or readily adapting methods described in U.S. Pat. Nos. 4,305,781, 4,753,710, and 6,270,626, which are incorporated in their entireties by reference herein. If necessary, dried bentonite ores can be pulverized by means of an attrition grinding machine, such as a centrifugal roller mill, or an impact mill, such as a hammer mill, sufficient to provide microparticle sizing and/or any desired particle distribution of microparticles.

**[0038]** The concentration of bentonite when used in an aqueous bentonite suspension, can be, for example, between about 0.1% and 10% by weight, or about 0.2 to about 5% by weight, or other ranges. The viscosity of an aqueous bentonite suspension is generally less than 500 mPa·s (measured using a Brookfield viscometer at 100 rpm).

**[0039]** The paper made in processes according to the present invention can comprise from about 0.05 to about 2.5 pounds (lb.) bentonite microparticles/ton dry fiber, about 0.1 to about 1 lb. bentonite microparticles/ton dry fiber, or about 0.2 to about 0.8 lb. bentonite microparticles/ton dry fiber (on a solids/solids basis). The amount of bentonite microparticles added, on a solids basis, can be expressed in weight percentage terms, wherein the amount of added bentonite microparticles can be as low as about 0.0025 wt % of the dry weight of the cellulose fibers, but usually does not exceed about 0.125% by weight. An amount of bentonite microparticles in the range of about 0.005 wt % to 0.1 wt % of the dry paper weight is more usual.

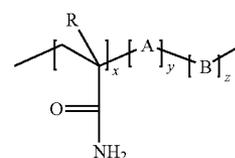
**[0040]** The silicon-containing microparticles can be added to paper pulp in combination with a glyoxalated polyacrylamide containing at least about 25% by weight cationic monomer in the wet-end of a papermaking process to improve retention and/or drainage. The paper made in processes according to the present invention can comprise from about 0.5 to about 12 pounds (lb.) polymer/ton dry fiber, about 1 pound to about 8 lb. polymer/ton dry fiber, or about 2 to about 6 lb. polymer/ton dry fiber (on a solids/solids basis). The amount of glyoxalated polyacrylamide polymer added, on a

solids basis, can be expressed in weight percentage terms, wherein the amount of added glyoxalated polyacrylamide polymer can be as low as about 0.03 wt % of the dry weight of the cellulose fibers, but usually does not exceed about 10% by weight. An amount of polymer in the range of about 0.1 wt % to 5 wt % of the dry paper weight is more usual.

**[0041]** The glyoxalated polyacrylamide polymers containing at least about 25% by weight cationic monomer can be introduced into the suspension undergoing treatment in high solids aqueous compositions thereof that are storage-stable at high polymer concentrations. The glyoxalated polyacrylamide compositions according to the present invention can have a solids concentration, for example, from about 1% and about 30%, by weight, or, for example, from about 5% to about 30%, by weight, or, for example, about 7% to about 15%, by weight or, for example, about 7% to about 13%, by weight.

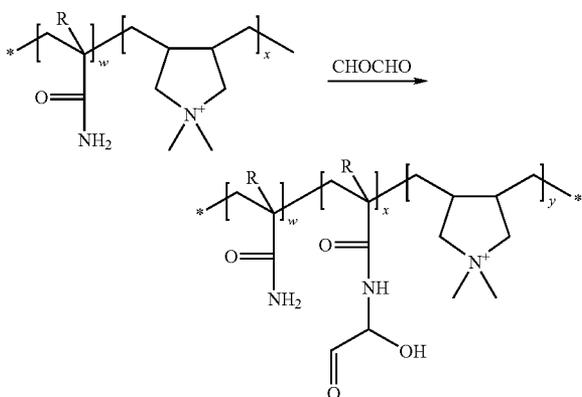
**[0042]** The glyoxalated acrylamide polymer according to the present invention can comprise, for example, from about 75% to about 10%, by weight, acrylamide monomer and from about 25% to about 90%, by weight, cationic monomer copolymerizable with the acrylamide monomer, and has sufficient glyoxal-reactive amide substituents and —CHOHCHO substituents to be thermosetting. The glyoxalated acrylamide polymer can comprise, for example, from about 70% to about 30%, by weight, acrylamide monomer and from about 30% to about 70%, by weight, cationic monomer, or, for example, from about 65% to about 50%, by weight, acrylamide monomer and from about 35% to about 50%, by weight, cationic monomer, or, for example, from about 62% to about 55%, by weight, acrylamide monomer and from about 38% to about 45%, by weight, cationic monomer.

**[0043]** A glyoxalated polyacrylamide polymer according to the present invention can incorporate a base polymer resin having the following exemplary formula



wherein R is H, C<sub>1</sub> alkyl, C<sub>2</sub> alkyl, C<sub>3</sub> alkyl, C<sub>4</sub> alkyl, or halogen; A is a cationic unit which imparts a charge to the resin polymer; B is an optional non-nucleophilic unit which does not react with glyoxal under aqueous condition; wherein the weight percent of x is from 75% to about 10%; the weight percent of y is from 25% to about 90%; the weight percent of z is from 0% to 65%; and the molecular weight of the base polymer resin is from 500 Daltons to 100,000 Daltons, or, for example, 3,000 Daltons to 20,000 Daltons, or, for example, 3,000 Daltons to 13,000 Daltons, or, for example, 5,000 Daltons to 9,000 Daltons.

**[0044]** These base polymer resins are glyoxalated to provide thermosetting resins that are particularly suitable for use as co-additives with silicon-containing microparticles for papermaking, increasing papermaking fiber retention and dewatering rate, and/or providing paper with good dry and temporary wet strength. The glyoxalation of polyacrylamide according to an exemplary illustration is schematically indicated below.



**[0045]** Glyoxal reacts with amide groups to form a pendant glyoxalated group. In addition, glyoxal cross-links the base polymer molecules at glyoxal-reactive amide substituents of the acrylamide units (not shown), leading to a thermosetting interpolymer and an associated increase of solution viscosity. The presence of high cationic monomer content in the resulting glyoxalated polyacrylamide polymers according to the present invention reduces the amide content and/or the cross-linking rate. Thus, the product can be prepared at a higher solid content but with longer shelf life. This higher charged glyoxalated polyacrylamide resin also gives comparable wet/dry strength in paper as commercially available 7.5% glyoxalated polyacrylamide products. As indicated, higher de-watering rates during the papermaking process are obtained by treating pulps with silicon-containing microparticles and the glyoxalated polyacrylamide polymer products of the present invention as compared to commercially available lower solids glyoxalated polyacrylamide polymer products.

**[0046]** Cationic monomers include, for example, 2-vinylpyridine, 2-vinyl-N-methylpyridinium chloride, (p-vinylphenyl)trimethyl ammonium chloride, diallyldimethylammonium chloride, 2-(dimethylamino)ethyl acrylate, trimethyl(p-vinylbenzyl)ammonium chloride, p-dimethylaminoethylstyrene, dimethylaminopropyl acrylamide, 2-methylacryloyloxyethyltrimethyl ammonium methylsulfate, and 3-acrylamido-3-methylbutyl trimethyl ammonium chloride.

**[0047]** The acrylamide can be replaced by other primary amide-containing monomers such as methacrylamide, ethylacrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide and the like. Thus, polyacrylamides, which by definition are polymers made from acrylamide monomers, include repeating units from at least one or more of these various compounds.

**[0048]** The acrylamide monomer provides the primary reaction sites on the base polymer backbone to which the glyoxal substituents are attached. The base polymer must have a sufficient number of base acrylamide monomers in its structure (pendant amide groups) so that, once functionalized with glyoxal, the resulting polymer is thermosetting. As used herein, "thermosetting" and "crosslinking", and similar terms are intended to embrace the structural and/or morphological change that occurs, for example, by covalent chemical reaction or ionic interaction between separate molecules in a composition. Generally, the amount of base acrylamide monomer should be at least about 10 weight percent of the

base polymer. Paper strengthening properties of the resulting polymer generally will increase with increased amounts of acrylamide content, although it has been found in the present invention that adequate dry strength properties can be provided in higher cationic monomer content polyacrylamide base polymers according to the present invention. The base acrylamide monomer is normally provided in an amount of at least about 50 weight percent and sometimes in excess of 60 weight percent of the total vinyl monomers from which the base polyacrylamide is prepared.

**[0049]** The base polymer optionally can also contain a non-nucleophilic monomer to reduce amide-glyoxal cross-linking reaction. The suitable non-nucleophilic monomers include vinyl acetate, N-vinylpyrrolidone, N,N-dimethylacrylamide, acrylonitrile, styrene, hydroxyl alkyl(meth)acrylates and the like. The weight percent of this non-nucleophilic unit can range from zero to 65 (e.g., 1 wt % to 80 wt %, 5 wt % to 70 wt %, 10 wt % to 60 wt %, 15 wt % to 50 wt %, 20 wt % to 40 wt % and so on).

**[0050]** The base polymer product of the copolymerization of the acrylamide monomer and cationic monomer for use in the present invention, or polyacrylamide base polymer, can be prepared by free radical polymerization in an aqueous system. Methods for making base polyacrylamide can be modified to practice the present invention. To prepare a polyacrylamide base polymer of a desired chemical composition and monomer distribution, the full complement of the cationic monomer(s) and the non-nucleophilic monomer(s) can be added all at once at the beginning of the polyacrylamide polymerization reaction. Alternatively, the cationic monomer(s) and the non-nucleophilic monomer(s) can be added continuously along with acrylamide monomer over the time course of the polymerization reaction. Still other options for reacting the cationic monomers and the non-nucleophilic monomers with the acrylamide monomer will be recognized by those skilled in the art, such as sequentially, batch, semi-batch, and the like. Commonly used free radical initiators that can be used in the present invention include various peroxide, azo compounds, potassium and ammonium persulfates, and a redox initiator system. The polyacrylamide base polymer has a molecular weight ranging, for example, from 500 Daltons to 100,000 Daltons, for example, from 3,000 Daltons to 20,000 Daltons, for example, from 3,000 Daltons to 13,000 Daltons, for example, from 5,000 Daltons to 9,000 Daltons. The molecular weight can be influenced by changing the reaction temperature, the level of solids in the reaction, the amount of initiator, the amount of chain transfer agent, and by other methods used by those skilled in the art. The suitable chain transfer agents include isopropyl alcohol, mercaptans, sodium formate, and sodium acetate.

**[0051]** The so-prepared base polymer can then be reacted with glyoxal, for instance, at a pH of 7 to 10. The weight ratio of the glyoxal to the base polymer ranges, for example, from about 0.01 to about 0.60:1, and for example, from about 0.10 to about 0.30:1, respectively. The reaction temperature can be maintained in the range of 15° C. to 50° C. A buffer can be added to control solution pH throughout the reaction. Suitable buffers include sodium phosphates, sodium pyrophosphate, borax, and Tris. Once the solution reaches a desired viscosity, dilute acid can be added to quench the reaction. The final pH of the solution can range from 2 to 5. Alternatively, either the glyoxal solution or the base polymer solution can be added to the reaction mixture slowly over time, or both the glyoxal and the base polymer solution can be added to the reaction mixture

ture slowly over time. Still other options for reacting glyoxal and base polymer can be used by those skilled in the art.

**[0052]** The compositions of the higher charged glyoxalated polyacrylamide polymers according to the present invention can be readily employed or stored for later use in the manufacture of paper as an aqueous solution. The compositions are highly storage stable, even at temperatures exceeding room temperature. As previously indicated, it is not necessary to add stabilizers or other storage-life promoting additives to the high solids polymer compositions according to the present invention to achieve significantly improved shelf life over conventional 7.5% glyoxalated polyacrylamide polymer formulations. The glyoxalated polyacrylamide polymer compositions according to the present invention do not need extraneous stabilizers, aldehyde scavengers, and/or surfactants, and the like, to achieve the improvements in storage stability, although these materials are not categorically excluded. The glyoxalated polyacrylamide polymer compositions of the present invention can contain no such stabilizer additives or can be essentially free of them (that is, contain <0.1 wt % total stabilizers, aldehyde scavengers, and surfactants).

**[0053]** The high solids glyoxalated acrylamide polymer compositions of the present invention can have a viscosity of less than about 45 cps (e.g., 1 cps to 24 cps, or 5 cps to 20 cps, or 10 cps to 20 cps), or particularly less than 25 cps, as measured on a Brookfield viscometer using #2 spindle at 60 rpm after 14 days storage at 37° C. The high solids glyoxalated acrylamide polymer composition can have a viscosity of less than about 25 cps, as measured on a Brookfield viscometer using #2 spindle at 60 rpm (e.g., 1 cps to 24 cps or 5 cps to 20 cps, or 10 cps to 20 cps) after 28 days storage at 37° C. These properties indicate very little if any gelling occurs in the polymer compositions according to the present invention within at least these storage periods and conditions.

**[0054]** The base polymer can have a charge density of 1.0 meg/g or greater, such as from about 1.0 to about 4.5 meg/g, such as from 1.1 to 4.5 meg/g or from 1.5 to 3.5 meg/g and the like. Improved and unexpected properties have been achieved especially in the range of from 1 to 4.5 meg/g.

**[0055]** The additive system combining glyoxalated polyacrylamide polymer and silicon-containing microparticles according to the present invention is not limited to treating any particular type of paper and should find application in all grades of paper, Kraft paper, sulfite paper, semichemical paper, and the like, including paper produced using bleached pulp, unbleached pulp, or combinations thereof. For example, the drainage and retention improvements due to the combination of the glyoxalated polyacrylamide polymers and silicon-containing microparticles according to the present invention can be observed in different types of pulps. For example, the pulp may comprise virgin and/or recycled pulp, such as virgin sulfite pulp, broke pulp, a hardwood kraft pulp, a softwood kraft pulp, old corrugated containers (OCC), mixtures of such pulps, and the like. There are a variety of mechanical pulping methods to which the present invention can be applied. For example, thermomechanical pulp (TMP) uses a combination of heated wood chips and mechanical processes. Stone Groundwood (SOW) grinds or macerates the wood chips. Chemithermomechanical pulp (CTMP) uses a variety of chemicals, heat, and grinding techniques to produce pulp. Different types of pulp require different types of paper although many papers can use a combination or "blend" of several different types of pulp and recycled/recovered paper. These pulp formulations can be referred to as fiber furnishes.

**[0056]** A paper product can be provided comprising the glyoxalated polyacrylamide polymer and silicon-containing microparticles of the present invention. The product may comprise at least one paper layer or web containing the glyoxalated polyacrylamide polymer and silicon-containing microparticles, for example, paper sheeting, liner board, newsprint, paperboard, tissue paper, fluting medium, and wall board.

**[0057]** The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention, in which all percentages, parts, ratios and the like are proportions by weight unless otherwise specified.

## EXAMPLES

**[0058]** In these experiments, the effects of a combination of high solids, higher charged glyoxalated polyacrylamide polymer and silicon-containing microparticles representing various non-limiting embodiments of the present invention on the de-watering rate and retention properties of an aqueous cellulosic suspension were compared to that of several commercial polyacrylamide and polyamine based additives in their as-supplied product forms and modified forms thereof.

**[0059]** Molecular weights of the base polymers of the polyacrylamide polymers were determined in the following manner. Polymer molecular weight was characterized using Waters Breeze System—Gel Permeation Chromatography (GPC). The elution solvent was an aqueous buffer solution containing 0.8 mole/L sodium nitrate and 0.1 mole/L acetic acid. In a typical GPC experiment, concentrated polymer sample was diluted with the elution solvent to give a final concentration of around 0.1%. The diluted polymer solution was injected into the system using a Waters 717plus Autosampler and pumped through a Waters Ultrahydrogel® Guard Column followed by a Waters Ultrahydrogel® Linear Column. The flow rate was 0.9 ml/min. The molecular weight distribution of the polymer sample was calculated based on a calibration curve determined using poly(ethylene glycol) standard GPC calibration kit from Polysciences.

### Example 1

#### Synthesis of Polyacrylamide Base Polymers

**[0060]** Into a reaction vessel equipped with reflux condenser, stirrer, and thermometer were added water, sodium formate, and a DADMAC aqueous solution (64 wt %). This portion of DADMAC added in the beginning of the reaction is referred to herein as "DADMAC 1". The vessel was then heated to 80° C. and maintained at this temperature. To the vessel were slowly added acrylamide aqueous solution (50%), DADMAC aqueous solution (64%), and ammonium persulfate. The addition time of acrylamide and diallyldimethylammonium chloride was 190 minutes and the addition time of ammonium persulfate was 220 minutes. The portion of DADMAC added over this 190 minute addition period is referred to herein as "DADMAC 2". The reaction mixture was then heated at 80° C. for an additional one hour and was then cooled to room temperature. Table 1 listed the addition dosages of all the compounds used in synthesizing the base polymers.

TABLE 1

Base polymer preparation dosages.									
	Water (g)	Sodium formate (g)	DADMAC 1 (g)	Acryl- amide (g)	DADMAC 2 (g)	Ammonium persulfate (g)	Total DADMAC (wt %)	Charge density (meq/g)	Weight average molecular weight (Da)
Base polymer 1	58.3	5.1	6	165	53	12.3 (14% in water)	32	2.0	8000
Base polymer 2	74	4.4	16	155	65	6.5 (23% in water)	40	2.5	8900
Base polymer 3	84.7	4.3	16	116	95	7.15 (23% in water)	55	3.1	7600
Base polymer for Bubond 376	NA	NA	NA	NA	NA	NA	9.5	0.6	NA

## Glyoxalation

**[0061]** The glyoxalation of the base polymers was conducted in the following manner. Into a reaction vessel were added water, base polymer, and sodium pyrophosphate. After 15 minutes of mixing, the pH of the reaction mixture was increased to 8.8 using 15% NaOH solution and the temperature of the mixture was maintained at 25° C. Once the viscosity of the mixture reached 15 cp, solution pH was lowered to 3.0 immediately using 25% H<sub>2</sub>SO<sub>4</sub>. The products were stored at 4° C. until further testing. Table 2 lists the dosages of all the compounds for glyoxalation. The products of these reactions were aqueous compositions containing the G-PAM polymers as active content therein. The numbering of the G-PAM products in Table 2 corresponds to the numbering of the Base polymers (see Table 1) used to synthesize the G-PAM product.

TABLE 2

Glyoxalation dosages.					
Product	Water (g)	Base polymer (g)	Glyoxal (40%) (g)	Sodium Pyrophosphate (g)	Final active content (wt %)
G-PAM1	143	47 (Base polymer1)	12	1.2	11.6%
G-PAM2	138	47 (Base polymer2)	13	1.2	12.0%
G-PAM3	128	57 (Base polymer3)	15	1.5	14.3%

## OCC Suspension De-Watering Test

**[0062]** In this test, the effect of different G-PAMs, with and without silicon-containing microparticles, on OCC (old corrugated cardboard) suspension de-watering rate and retention was studied. Pulp stock was post-refining recycled old corrugated cardboard (OCC) obtained from National Gypsum Company Pryor Papermaking Mill. For comparison, high solid G-PAM samples combined with silicon-containing microparticles were tested against commercial products BUBOND® 376 (Buckman International) and BUFLOC® 5031 (Buckman International). BUBOND® 376 is a conventional G-PAM product with 7% active content and its base-polymer has 9.5 wt % DADMAC. BUFLOC® 5031 is a polyamine product which has been widely applied as a coagulant to improve paper retention drainage.

**[0063]** In a typical test, 800 mL 1.0% OCC suspension was added to a Mutek DFR-4 drainage/retention tester and was then mixed at 900 rpm. G-PAM or polyamine was added five seconds before the addition of commercial cationic polyacrylamide flocculant BUFLOC® 5511. Five seconds after the addition of BUFLOC® 5511, mixing rate was lowered to 650 rpm. If applicable, a silicon-containing microparticulate retention aid, silica NP 890 (EKA), was added immediately after the mixing rate was lowered to 650 rpm. In Table 3, dosages of components are described in terms of pounds (lb) component/ton dry fiber. After another five seconds, the mixing was stopped and 400 mL filtrate was allowed to pass through a 60 mesh wire. A higher drainage rate indicates a faster production rate, which can translate into a lower energy consumption during the paper drying process. Filtrate turbidity was recorded using a HACH 2100 turbidimeter. A lower turbidity indicates a higher retention efficiency.

TABLE 3

Retention and drainage test results.			
Sample	Additives and Dosages	Filtrate turbidity (ntu)	400 mL drainage time (s)
1	0.5 lb/ton BUFLOC ® 5511	512	42
2	5 lb/ton BUFLOC ® 5031 + 0.5 lb/ton BUFLOC ® 5511	346	39.8

TABLE 3-continued

Retention and drainage test results.			
Sample	Additives and Dosages	Filtrate turbidity (ntu)	400 mL drainage time (s)
3	5 lb/ton BUBOND® 376 + 0.5 lb/ton BUFLOC® 5511	498	41.5
4	5 lb/ton G-PAM1 + 0.5 lb/ton BUFLOC® 5511	306	37.7
5	5 lb/ton G-PAM2 + 0.5 lb/ton BUFLOC® 5511	320	37.9
6	5 lb/ton G-PAM3 + 0.5 lb/ton BUFLOC® 5511	330	39
7	5 lb/ton BUFLOC® 5031 + 0.5 lb/ton BUFLOC® 5511 + 0.5 lb/ton silica	318	28.5
8	5 lb/ton BUBOND® 376 + 0.5 lb/ton BUFLOC® 5511 + 0.5 lb/ton silica	481	38
9	5 lb/ton G-PAM1 + 0.5 lb/ton BUFLOC® 5511 + 0.5 lb/ton silica	295	29
10	5 lb/ton G-PAM2 + 0.5 lb/ton BUFLOC® 5511 + 0.5 lb/ton silica	297	30
11	5 lb/ton G-PAM3 + 0.5 lb/ton BUFLOC® 5511 + 0.5 lb/ton silica	304	28.3
12	5 lb/ton BUFLOC® 5031 + 0.5 lb/ton BUFLOC® 5511 + 0.75 lb/ton silica	340	24.6
13	5 lb/ton G-PAM1 + 0.5 lb/ton BUFLOC® 5511 + 0.75 lb/ton silica	259	24.9
14	5 lb/ton G-PAM2 + 0.5 lb/ton BUFLOC® 5511 + 0.75 lb/ton silica	274	24.3
15	5 lb/ton G-PAM3 + 0.5 lb/ton BUFLOC® 5511 + 0.75 lb/ton silica	301	23.4

**[0064]** As shown in Table 3, the addition of silica microparticles increased retention/drainage performance significantly of all three high solids G-PAM products. Further, all three high solids G-PAM products, when used in combination with silica microparticles, provided much lower filtrate turbidities and faster drainage rate than the conventional commercial G-PAM product BUBOND® 376, with or without the silica. Furthermore, all three high solids G-PAM products, when used in combination with silica microparticles, also provided lower filtrate turbidities and comparable drainage rate than the commercial coagulant BUFLOC® 5031, with or without the silica. In view of these showings, it is further believed that high solids G-PAM products, when used in combination with silica microparticles, can be applied to replace both conventional G-PAM products as dry strength resin and also conventional polyamine products as coagulant.

**[0065]** Applicants specifically incorporate the entire contents of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

**[0066]** Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

What is claimed is:

1. A process for making paper comprising adding silicon-containing microparticles and a glyoxalated polyacrylamide polymer comprising at least about 25% by weight cationic monomer to an aqueous suspension containing cellulose fibers, and forming said suspension into a water-laid web and drying said web to form paper, wherein the added amount of silicon-containing microparticles is effective to increase fiber retention and de-watering rate as compared to paper made with the suspension absent the silicon-containing microparticles.

2. The process of claim 1, wherein the glyoxalated polyacrylamide polymer is a reaction product of glyoxal and a base polymer comprising the acrylamide monomer and the cationic monomer.

3. The process of claim 2, wherein said base polymer has an average molecular weight range from 500 Daltons to 20,000 Daltons.

4. The process of claim 2, wherein said base polymer has a charge density of 1 meg/g or greater.

5. The process of claim 2, wherein said base polymer has a charge density of from 1 meg/g to 4.5 meg/g.

6. The process of claim 2, wherein said base polymer has a charge density of from 1.5 to 3.5 meg/g.

7. The process according to claim 1, wherein the paper comprises from about 0.05 to about 2.5 pounds said silicon-containing microparticles/ton dry fiber.

8. The process according to claim 1, wherein the silicon-containing microparticles are selected from silica microparticles and bentonite microparticles.

9. The process according to claim 1, wherein the silicon-containing microparticles comprise amorphous silica microparticles.

10. The process according to claim 1, wherein said silicon-containing microparticles comprise colloidal silica comprising a surface area from 300 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g and an S-value of from 80% to 20%.

11. The process according to claim 1, wherein said silicon-containing microparticles comprise bentonite microparticles.

12. The process according to claim 1, wherein the microparticles have an absolute particle size of not greater than about 750 nm.

13. The process according to claim 1, wherein at least 90% of the microparticles have an absolute particle size of not greater than about 750 nm.

14. The process according to claim 1, wherein the paper comprises from about 0.5 to about 12 pounds said polymer/ton dry fiber.

15. The process according to claim 1, wherein said adding comprises introducing an aqueous polymer composition comprising said glyoxalated polyacrylamide polymer, wherein the polymer composition comprises (a) at least 10%, by weight, said glyoxalated polyacrylamide polymer, and (b) water, wherein the glyoxalated polyacrylamide polymer comprises a reaction product between glyoxal and a cationic polyacrylamide base polymer, wherein the cationic polyacrylamide base polymer comprises from about 75% to about 10%, by weight, acrylamide monomer and from about 25% to about 90%, by weight, cationic monomer copolymerizable with said acrylamide monomer, and having sufficient glyoxal-reactive amide substituents and —CHOHCHO substituents to be thermosetting.

16. The process according to claim 15, wherein said polymer composition comprising about 5% to about 30%, by weight, said glyoxalated polyacrylamide polymer.

17. The process according to claim 15, wherein said polymer composition comprising about 7% to about 15%, by weight, said glyoxalated polyacrylamide polymer.

18. The process according to claim 15, wherein the cationic monomer is 2-vinylpyridine, 2-vinyl-N-methylpyridinium chloride, (p-vinylphenyl) trimethyl ammonium chloride, diallyldimethylammonium chloride, 2-(dimethylamino)

ethyl acrylate, trimethyl(p-vinylbenzyl)ammonium chloride, p-dimethylaminoethylstyrene, dimethylaminopropyl acrylamide, 2-methylacryloyloxyethyltrimethyl ammonium methylsulfate, or 3-acrylamido-3-methylbutyl trimethyl ammonium chloride, or any combination thereof.

19. The process according to claim 15, wherein the cationic monomer is diallyldimethyl-ammonium chloride.

20. The process according to claim 15, wherein the acrylamide monomer is acrylamide, methacrylamide, ethylacrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, or N-ethyl methacrylamide, or any combination thereof.

21. The process according to claim 15, wherein the cationic polyacrylamide base polymer comprises from about 70% to about 20%, by weight, acrylamide monomer and from about 30% to about 80%, by weight, cationic monomer copolymerizable with said acrylamide monomer.

22. The process according to claim 15, wherein the polymer is a reaction product of glyoxal and a base polymer comprising the acrylamide monomer and the cationic monomer in a weight ratio ranging from about 0.01 to 0.6:1.

23. The process according to claim 22, wherein the base polymer has a molecular weight ranging from about 500 Daltons to about 100,000 Daltons.

24. The process according to claim 1, wherein the paper comprises a cellulosic fibrous non-woven web.

25. A product comprising a paper made by the process of claim 1 containing the glyoxalated polyacrylamide polymer and silicon-containing microparticles.

26. A product according to claim 25, wherein the product is paper sheeting, paperboard, tissue paper, or wall board.

27. A product according to claim 25, wherein the product is newsprint or linerboard.

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