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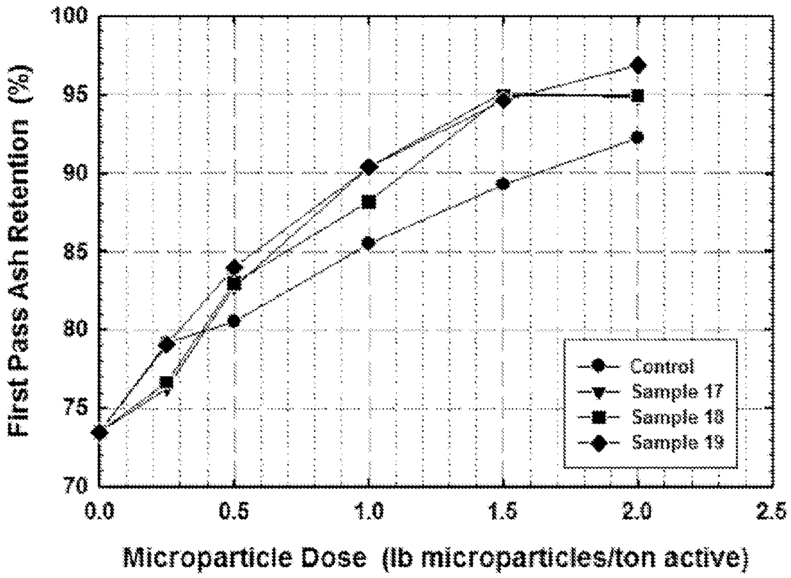
(54) Titre : PRODUIT DE SILICE COLLOIDALE AQUEUSE STABLE, ET SES PROCEDES DE FABRICATION ET D'UTILISATION
(54) Title: STABLE AQUEOUS COLLOIDAL SILICA PRODUCT, AND METHODS TO MAKE AND USE SAME



(57) Abrégé/Abstract:
An aqueous colloidal silica product, a method of using the aqueous colloidal silica product, and a method of producing an aqueous colloidal silica product, are disclosed. The method of producing the aqueous colloidal silica product incorporates semi-batch addition of alkali metal silicate, which is capable of achieving an aqueous colloidal silica product having desirable physical and chemical characteristics. The aqueous colloidal silica product has been found to be particularly useful as an additive in a papermaking process.

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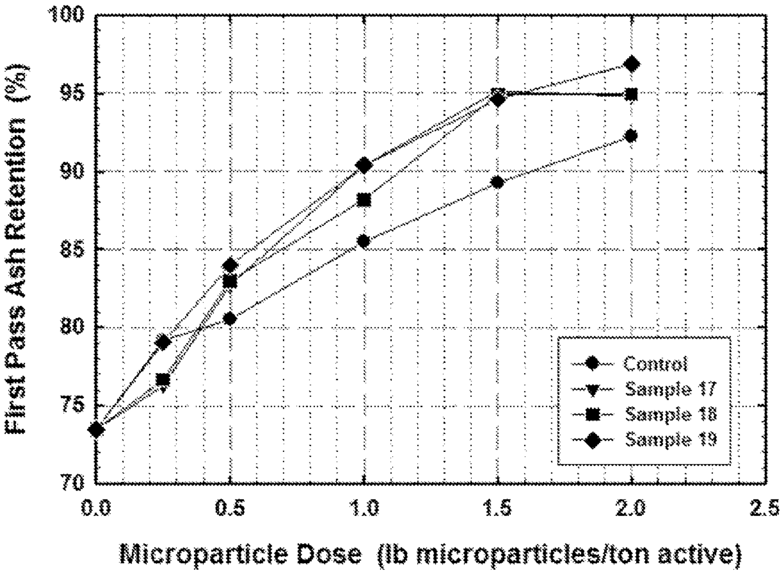
(54) Title: STABLE AQUEOUS COLLOIDAL SILICA PRODUCT, AND METHODS TO MAKE AND USE SAME

FIG. 1



(57) Abstract: An aqueous colloidal silica product, a method of using the aqueous colloidal silica product, and a method of producing an aqueous colloidal silica product, are disclosed. The method of producing the aqueous colloidal silica product incorporates semi-batch addition of alkali metal silicate, which is capable of achieving an aqueous colloidal silica product having desirable physical and chemical characteristics. The aqueous colloidal silica product has been found to be particularly useful as an additive in a papermaking process.

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STABLE AQUEOUS COLLOIDAL SILICA PRODUCT, AND METHODS TO MAKE AND USE SAME

FIELD

[0001] At least one embodiment of the invention is directed to colloidal silica sols having high solids contents and low viscosity, while maintaining high surface area and enhanced stability. It is also directed to a new process involving a semi-batch addition for making such colloidal silica sols and to the use of such colloidal silica sols in a production of paper. At least one embodiment of the invention is directed to an aqueous colloidal silica product, a method of using an aqueous colloidal silica product, and a method of producing an aqueous colloidal silica product. The aqueous colloidal silica product is stable and has a lower viscosity than thought to be achievable for products having a colloidal silica solids concentration ranging from 16–18% by weight (*i.e.*, 16–18% by weight of SiO_2 solids) and produced via conventional production methods.

BACKGROUND

[0002] This present invention is directed to colloidal silica sols having high solids contents and low viscosity, while maintaining high surface area and enhanced stability. It is also directed to a new process involving a semi-batch addition for making such colloidal silica sols and to the use of such colloidal silica sols in a production of paper. The colloidal silica sols of the present invention uniquely exhibit high solids contents in the range between about 16 to about 18% by weight of SiO_2 solids, with viscosity ranging from about 4 to about 20 cPs, while the said colloidal silica sols still maintain high surface area and enhanced stability without modification of the surface with, for example, aluminum. Moreover the colloidal sols of the invention is prepared via a new semi-batch process, which is different from conventional silica sols process such as described in U.S. Pat. Nos. 6,372,806 and 6,372,089. Furthermore, the colloidal silica sols of the present invention advantageously exhibit excellent activity in many papermaking furnishes. The silica sols of present invention are useful, among other areas, in the papermaking industry, for example, as retention and dewatering aids.

[0003] In contrast, the present invention provides a stable composition of colloidal silica sols that have concentration ranging from about 16 to about 18 percent by weight of SiO_2 solids with low viscosity ranging from about 4 to about 20 cps, which is not in the teachings of the above reference patents. The present invention provides stable silica colloidal sols with high surface area and enhanced stability without modify the surface with aluminum, as described in U.S. Pat. 5,368,833.

BRIEF SUMMARY

[0004] In a first exemplary embodiment, the disclosure is directed to a stable aqueous colloidal silica product. The colloidal silica sols can be produced and stored at concentrations of about16 to about 18 percent by weight of SiO_2 solids, and remain stable at room temperature for at least 30 days, typically for at least 180 days. The aqueous colloidal silica product has a viscosity ranging from about 4 to about 20 cps and an S-value ranging from 26 to 40%. The colloidal silica solids have a specific surface area ranging from 700 to 850 m^2/g.

[0005] In a second exemplary embodiment, the disclosure is directed to a method of producing an aqueous colloidal silica product. The method comprises, first, charging a reaction vessel with a cationic ion exchange resin having at least 40 percent, preferably at least 50 percent of its ion exchange capacity in the hydrogen form wherein the reaction vessel has, for example a screen near the bottom of the reaction vessel, for separating the colloidal silica formed during the process from ion exchange resin. Second, charging the reaction vessel with water and stirring the contents of the reaction vessel. Third, adjusting the temperature of the contents of the said reaction vessel to be in the range from 70 to 200 degrees Fahrenheit, preferably in the range from 100 to 160 degrees Fahrenheit. Fourth, adding a first quantity of alkali metal silicate to the said water and cationic ion exchange resin under agitation, thereby forming a first intermediate composition comprising a first portion of aqueous colloidal silica product. Fifth, after 0 to 90 minutes, a second quantity of alkali metal silicate is added to the first intermediate composition under agitation, thereby forming a second intermediate composition comprising a second portion of aqueous colloidal silica product. After about 0 minutes to 24 hours, the first and second portions of aqueous colloidal silica products are separated from the second intermediate composition, thereby producing the aqueous colloidal silica product. The first and second quantity of alkali metal silicate comprise a total quantity, with the first quantity ranging from 60 to 95 weight percent of the total quantity. The first intermediate composition has a temperature ranging from 70 to 200 degrees Fahrenheit and a pH ranging from 8 to 14. The first quantity of alkali metal silicate is added at a first rate sufficient to allow the first addition to last for 1 to 45 minutes. The second intermediate composition has a temperature ranging from 70 to 200 degrees Fahrenheit and a pH ranging from 9 to 11. The second quantity of alkali metal silicate is added at a second rate sufficient to allow the second addition to last for 5 to 120 minutes.

[0006] In a third exemplary embodiment, the disclosure is directed to a method of making a cellulosic sheet. The method comprises preparing a cellulosic furnish containing from 0.01 to 1.5 weight percent cellulosic fiber. An amount of aqueous colloidal silica product as described in the first exemplary embodiment is added to the cellulosic furnish. The amount of aqueous colloidal silica product is sufficient to achieve a concentration of colloidal silica solids of from about 0.00005 to about 1.5 weight percent per dry weight of fiber in the cellulosic furnish. An amount of a water soluble polymeric flocculant is added to the cellulosic furnish. The amount of water soluble polymeric flocculant is sufficient to achieve a concentration of water soluble polymeric flocculant of from about 0.001 to about 5 weight percent per dry weight of fiber in the cellulosic furnish. The water soluble polymeric flocculant has a molecular weight ranging from 500,000 to 30 million daltons. The cellulosic furnish is then dewatered to obtain a cellulosic sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The advantages of the present disclosure will become more readily apparent to those of ordinary skill in the relevant art after reviewing the following detailed description and accompanying drawing, wherein:

[0008] FIG. 1 is a graph illustrating the improved first pass ash retention of three batches that incorporate the inventive aqueous colloidal silica product of the present disclosure, as compared to a control sample.

DETAILED DESCRIPTION

[0009] While embodiments encompassing the general inventive concepts may take various forms, there will hereinafter be described various embodiments with the understanding the general inventive concepts are not intended to be limited to the disclosed embodiments.

[0010] All percentages, parts and ratios as used herein, are by weight of the total product, unless specified otherwise. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include solvents or by-products that may be included in commercially available materials, unless specified otherwise.

[0011] All references to singular characteristics or limitations of the present disclosure shall include the corresponding plural characteristic or limitation, and vice versa, unless otherwise specified or clearly implied to the contrary by the context in which the reference is made.

[0012] All combinations of method or process steps as used herein can be performed in any order, unless otherwise specified or clearly implied to the contrary by the context in which the referenced combination is made.

[0013] All ranges and parameters, including but not limited to percentages, parts, and ratios, disclosed herein are understood to encompass any and all sub-ranges assumed and subsumed therein, and every number between the endpoints. For example, a stated range of "1 to 10" should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more *(e.g., 1* to 6.1) and ending with a maximum value of 10 or less *(e.g.,* 2.3 to 9.4, 3 to

8, 4 to 7), and finally to each number 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 contained within the range.

[0014] Ordinal numbers (*e.g.*, first, second, third, etc.) may be utilized herein to describe various aspects of the present disclosure that may be similar. For example, two adding steps may be defined using ordinal numbers (*e.g.*, "first adding" and "second adding"). When utilized, the ordinal numbers are used for the purposes of differentiating one element from another similarly-named element, thereby allowing for clarity in referencing the similarly-named elements. The ordinal numbers should not be construed as necessarily limiting the order of elements, unless clearly defined by the context of the disclosure.

[0015] The various embodiments of the compositions and products of the present disclosure may also be substantially free of any optional ingredient or feature described herein, provided that the remaining composition or product still contains all of the required ingredients or features as described herein. In this context, and unless otherwise specified, the term "substantially free" means that the selected composition or product contains less than a functional amount of the optional ingredient, typically less than about 1%, including less than about 0.5%, including less than about 0.1%, and also including zero percent, by weight of such optional ingredient.

[0016] The compositions and products may comprise, consist of, or consist essentially of the required elements of the products as described herein, as well as any additional or optional element described herein or otherwise useful in product applications.

[0017] The term "aqueous" as used herein, unless otherwise specified, is intended to be construed as a modifier that means "water-containing" or "in water," as opposed to "oil-containing" or "in oil." For purposes of this disclosure, "water" refers to liquid water. An aqueous composition may be liquid water, a solution having liquid water as a solvent, or a slurry of solids in liquid water. Notably, a silica sol is an aqueous composition, as it comprises colloidal silica solids in liquid water.

[0018] The term “colloid” as used herein, unless otherwise specified, is intended to be construed as a substance containing ultra-small particles substantially evenly dispersed throughout another substance. The colloid consists of two separate phases: a dispersed phase (or internal phase) and a continuous phase (or dispersion medium) within which the dispersed phase particles are dispersed. The dispersed phase particles may be solid, liquid, or gas. The dispersed-phase particles may have a diameter ranging from about 1 to 1,000,000 nanometers. The colloid may be substantially affected by the surface chemistry present in the dispersed-phase particles. An exemplary embodiment of a colloid is an aqueous colloidal silica product. Exemplary embodiments of dispersed-phase particles are colloidal silica solids.

[0019] The term “colloidal silica” as used herein, unless otherwise specified, is intended to be construed as a colloid in which the primary dispersed-phase particles comprise silicon containing molecules. This definition includes the full teachings of the reference book: *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*, by Ralph K. Iler, John Wiley and Sons, Inc. (1979), in general, and particularly pages 312–599. When the particles have a diameter of above 100 nm, the particles may be referred to as “sols,” “silica sols,” “aquasols,” or “nanoparticles.”

[0020] The term “product” as used herein, unless otherwise specified, is intended to be construed as a substance that is created from a chemical reaction or a series thereof and capable of being utilized as an ingredient in a manufacturing process. As used herein, a “product” is generally a portion of the composition that results from the chemical reaction or series thereof.

[0021] The term “aqueous colloidal silica product” (or “AqCSP”) as used herein, unless otherwise specified, is intended to be construed as a homogenous mixture with dispersed silica particles/aggregates in aqueous phase that were created from a chemical reaction or a series thereof, and capable of being utilized as an ingredient in a manufacturing process, particularly in a papermaking process. In certain embodiments, an “aqueous colloidal silica product” is a silica sol.

[0022] The term "silica sol" as used herein, unless otherwise specified, is intended to be construed as a homogenous aqueous mixture composition containing colloidal silica particles or aggregates.

[0023] In the event that the above definitions or a description stated elsewhere in this application is inconsistent with a meaning (explicit or implicit) which is commonly used, in a dictionary, or stated in a source incorporated by reference into this application, the application and the claim terms in particular are understood to be construed according to the definition or description in this application, and not according to the common definition, dictionary definition, or the definition that was incorporated by reference. In light of the above, in the event that a term can only be understood if it is construed by a dictionary, if the term is defined by the Kirk-Othmer Encyclopedia of Chemical Technology, 5th Edition, (2005), (Published by Wiley, John & Sons, Inc.) this definition shall control how the term is to be defined in the claims.

[0024] In at least one embodiment colloidal silica sols uniquely exhibit high solids contents in the range between about 16 to about 18% by weight of SiO_2 solids, with viscosity ranging from about 4 to about 20 cPs, while the said colloidal silica sols still maintain high surface area and enhanced stability without modification of the surface with, for example, aluminum. Moreover the colloidal sols of the invention is prepared via a new semi-batch process, which is different conventional silica sols process such as described in US Patents 5,368,833, 6,372,806 and 6,372,089. Furthermore, the colloidal silica sols of the present invention advantageously exhibit excellent activity in many papermaking furnishes. The silica sols of present invention are useful, among other areas, in the papermaking industry, for example, as retention and dewatering aids.

[0025] At least one embodiment is a stable composition of colloidal silica sols that have concentration ranging from about 16 to about 18 percent by weight of SiO_2 solids with low viscosity ranging from about 4 to about 20 cps, which is not accomplished according to the teachings of the above reference patents. In particular the sol may exclude the presence of aluminum yet has as high or higher surface area and/or is as stable, or more stable than those sols described in US Patent 5,368,833.

[0026] At least one embodiment is directed to an aqueous colloidal silica product. The aqueous colloidal silica product comprises water and from 16 to 18 weight percent colloidal silica solids. The aqueous colloidal silica product has a viscosity ranging from about 4 to about 20 cps and an S-value ranging from 26 to 40%. The colloidal silica solids have a specific surface area ranging from 700 to 850 m^2/g.

[0027] At least one embodiment is directed to a method of producing an aqueous colloidal silica product. The method comprises, first, charging a reaction vessel with a cationic ion exchange resin having at least 40 percent, preferably at least 50 percent of its ion exchange capacity in the hydrogen form wherein the reaction vessel has for example a screen near the bottom of the reaction vessel, for separating the colloidal silica formed during the process from ion exchange resin. Second, charging the reaction vessel with water and stirring the contents of the reaction vessel. Third, adjusting the temperature of the contents of the said reaction vessel to be in the range from 70 to 200 degrees Fahrenheit, preferably in the range from 100 to 160 degrees Fahrenheit. Fourth, adding a first quantity of alkali metal silicate to the said water and cationic ion exchange resin under agitation, thereby forming a first intermediate composition comprising a first portion of aqueous colloidal silica product. Fifth, after 0 to 90 minutes, a second quantity of alkali metal silicate is added to the first intermediate composition under agitation, thereby forming a second intermediate composition comprising a second portion of aqueous colloidal silica product. After about 0 minutes to 24 hours, the first and second portions of aqueous colloidal silica products are separated from the second intermediate composition, thereby producing the aqueous colloidal silica product. The first and second quantity of alkali metal silicate comprise a total quantity, with the first quantity ranging from 60 to 95 weight percent of the total quantity. The first intermediate composition has a temperature ranging from 70 to 200 degrees Fahrenheit and a pH ranging from 8 to 14. The first quantity of alkali metal silicate is added at a first rate sufficient to allow the first addition to last for 1 to 45 minutes. The second intermediate composition has a temperature ranging from 70 to 200 degrees Fahrenheit and a pH ranging from 9 to 11. The second quantity of alkali metal silicate is added at a second rate sufficient to allow the second addition to last for 5 to 120 minutes.

[0028] At least one embodiment is directed to a method of making a cellulosic sheet. The method comprises preparing a cellulosic furnish containing from 0.01 to 1.5 weight percent cellulosic fiber. An amount of aqueous colloidal silica product as described in the first exemplary embodiment is added to the cellulosic furnish. The amount of aqueous colloidal silica product is sufficient to achieve a concentration of colloidal silica solids of from about 0.00005 to about 1.5 weight percent per dry weight of fiber in the cellulosic furnish. An amount of a water soluble polymeric flocculant is added to the cellulosic furnish. The amount of water soluble polymeric flocculant is sufficient to achieve a concentration of water soluble polymeric flocculant of from about 0.001 to about 5 weight percent per dry weight of fiber in the cellulosic furnish. The water soluble polymeric flocculant has a molecular weight ranging from 500,000 to 30 million daltons. The cellulosic furnish is then dewatered to obtain a cellulosic sheet.

[0029] At least one embodiment is directed to an aqueous colloidal silica product having certain chemical and physical characteristics. While a person of skill in the art will readily recognize that the methods of the second exemplary embodiment may be used to produce the first exemplary embodiment, the first exemplary embodiment should not be construed as limited to the method of the second exemplary embodiment. In other words, the aqueous colloidal silica product may be produced by methods that differ from those of the second embodiment.

[0030] In at least one embodiment the aqueous colloidal silica product comprise colloidal silica solids at a concentration ranging from 16 to 18 weight percent, or 16 to 17, or 17 to 18, of the aqueous colloidal silica product. In certain exemplary embodiments, the aqueous colloidal silica product comprises colloidal silica solids at a concentration of at least 16 weight percent, or at least 16.2 weight percent, or at least 16.5 weight percent, or at least 16.6 weight percent, or at least 16.7 weight percent, or at least 16.8 weight percent, or at least 16.9 weight percent, or at least 17 weight percent, up to 18 weight percent.

[0031] Viscosity of the aqueous colloidal silica product is a parameter that can be important to the manufacturers and users of aqueous colloidal silica products. The aqueous colloidal silica products need to flow through the cationic resin bed and pipes with relative ease in order to be useful in manufacturing processes. According to the first exemplary embodiment of the present disclosure, the aqueous colloidal silica product has a viscosity ranging from about 4 to about 20 cps. In certain embodiments, the aqueous colloidal silica product has a viscosity of at least about 4 cps, and up to 20 cps, or up to 18 cps, or up to 15 cps, or up to 12 cps, or up to 10 cps, or up to 8 cps. In certain embodiments, the aqueous colloidal silica product has a viscosity ranging from 4 to 18 cps, or 4 to 15 cps, or 4 to 10 cps.

[0032] The S-value of the aqueous colloidal silica product is another parameter that may be monitored and reported to users of aqueous colloidal silica products. S-value is a quantification of the degree of microaggregation of colloidal materials. The exact definition of S-value can be found in *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*, by Ralph K. Iler, John Wiley and Sons, Inc. (1979). According to the first exemplary embodiment of the present disclosure, the aqueous colloidal silica product has an S-value ranging from 26 to 40%. In certain embodiments, the aqueous colloidal silica product has an S-value of at least 26%, or at least 27%, or at least 28%, or at least 29%, and up to 40%, or up to 39%, or up to 38%, or up to 37%, or up to 36%, or up to 35%, or up to 34%, or up to 33%, or up to 32%, or up to 31%, or up to 30%. In certain embodiments, the aqueous colloidal silica product has an S-value ranging from 28 to 40%, or 29 to 39%.

[0033] Specific surface area of the colloidal silica solids in an aqueous colloidal silica product is a parameter that may be monitored and reported to users of the aqueous colloidal silica product. Specific surface area is reported in units of area per weight or mass of a substance (*e.g.*, m^2/g). The first exemplary embodiment of the present disclosure comprises colloidal silica solids having a specific surface area ranging from 700 to 850 m^2/g. In certain embodiments, the aqueous colloidal silica product comprises colloidal silica solids having a specific surface area of at least 700 m^2/g, or at least 750 m^2/g, or at least 800 m^2/g, and up to 850 m^2/g. In certain embodiments, the colloidal silica solids of the aqueous colloidal silica product have a specific surface area ranging from 750 to 850 m^2/g, or 800 to 850 m^2/g.

[0034] The aqueous colloidal silica products may be considered to be stable for at least 30 days. In certain embodiments, the aqueous colloidal silica product is stable for at least 60 days, or at least 90 days, or at least 120 days, or at least 180 days, and, in certain embodiments, up to 360 days or more. In certain embodiments, the aqueous colloidal silica product is stable for 30 to 360 days, or from 60 to 360 days, or from 90 to 360 days, or 120 to 360 days, or 180 to 360 days. By "stable," it is meant that the aqueous colloidal silica product retains its physical and chemical properties related to one or more of weight percent colloidal silica solids, viscosity, S-value, and specific surface area at least at the broadest levels defined herein, even in the event that the aqueous colloidal silica product is no longer agitated. In other words, the aqueous colloidal silica product does not substantially degrade or lose its ability to be used in a manufacturing process, such as a papermaking process.

[0035] Aluminum or aluminum-containing compounds are sometimes added to aqueous colloidal silica products to treat the surface area of the colloidal silica solids, thereby stabilizing the aqueous colloidal silica product. The embodiments of the aqueous colloidal silica product disclosed herein are generally aluminum-free and do not need to be treated with aluminum or aluminum-containing compounds in order to maintain their stability. In certain embodiments, the aqueous colloidal silica product is aluminum-free and stable for at least 30 days, or at least 60 days, or at least 90 days, or at least 120 days, or at least 180 days, and up to 360 days. In certain embodiments, the aqueous colloidal silica product is stable for 30 to 360 days, or from 60 to 360 days, or from 90 to 360 days, or 120 to 360 days, or 180 to 360 days. The term "aluminum-free" indicates that the aqueous colloidal silica product contains no more than trace amounts of aluminum or aluminum-containing compounds, *e.g.*, less than 500 ppm aluminum.

[0036] In certain embodiments of the aqueous colloidal silica product, the aqueous colloidal silica product further comprises an alkali metal or alkali metal-containing compound. The alkali metal or alkali metal-containing compound may be in the form of an alkali metal ion, an alkali metal oxide, an alkali metal silicate, an alkali metal salt, or another form known to those of skill in the art. A suitable alkali metal-containing compound used to make certain embodiments of the aqueous colloidal silica product is an alkali metal silicate, as described herein. Exemplary embodiments of alkali metals that may be present in the aqueous colloidal silica product include sodium, potassium, lithium and combinations thereof. Certain embodiments of the aqueous colloidal silica product further comprise a sodium-containing compound.

[0037] In embodiments of the aqueous colloidal silica product that further comprise an alkali metal or alkali metal-containing compound, the alkali metal or alkali metal-containing compound may be present in the aqueous colloidal silica product in an amount sufficient to provide a molar ratio of silica to alkali metal ranging from 5:1 to 50:1, or 5:1 to 30:1, or 5:1 to 25:1, or 5:1 to 20:1, or 5:1 to 15:1. In certain embodiments, the aqueous colloidal silica product has a molar ratio of SiO_2 to alkali metal of at least 8:1 and up to 50:1, or up to 30:1, or up to 25:1, or up to 20:1, or up to 15:1.

[0038] Certain embodiments of the aqueous colloidal silica product have a pH ranging from 9 to 11. The pH of the aqueous colloidal silica product may further range from 10 to 11.

[0039] At least one embodiment is directed to a method of producing an aqueous colloidal silica product. In an embodiment any of the above method(s) may be utilized to produce the aqueous colloidal silica product of the first exemplary embodiment of the present disclosure. However, the above methods are not limited so as to only produce only the above aqueous colloidal silica product. Furthermore, because the addition of the alkali metal silicate is performed in two steps, the method of producing an aqueous colloidal silica product may be described as "semi-batch" as opposed to "batch."

[0040] In at least one embodiment a first quantity of alkali metal silicate is added to water and a partially regenerated cationic ion exchange resin under agitation and at a temperature ranging from 70 to 200 degrees Fahrenheit, thereby forming a first intermediate composition comprising a first portion of aqueous colloidal silica product. The first intermediate composition has a pH of 8 to 14, or 8 to 12, or 9 to 11, and in certain embodiments, a pH of at least 8, or at least 9 or at least 10, and up to 14, or up to 13, or up to 12, or up to 11. The first quantity of alkali metal silicate is added to the water and cationic ion exchange resin at a rate sufficient to allow the addition to last for 1 to 45 minutes, or 2 to 30 minutes, and in certain embodiments, for at least 1, or at least 2 minutes, and up to 45, or up to 30, or up to 20, or up to 10 minutes.

[0041] After the first quantity of the alkali metal silicate is added, a second quantity of alkali metal silicate is added to the first intermediate composition under agitation and at a temperature ranging from 70 to 200 degrees Fahrenheit, thereby forming a second intermediate composition comprising a second portion of aqueous colloidal silica product. The second quantity may be added at any time from just after the addition of the first quantity of alkali metal silicate is completed (*e.g.*, 0 minutes), up to 90 minutes after the addition of the first quantity. The second intermediate composition has a pH ranging from 8 to 11, or from 9 to 11. The second quantity of alkali metal silicate is added at a second rate sufficient to allow the addition to last for 5 to 120 minutes, or 10 to 60 minutes, and in certain embodiments, for at least 5 minutes, or at least 10 minutes, or at least 15 minutes, up to 120 minutes, or up to 90 minutes, or up to 60 minutes, or up to 45 minutes, or up to 30 minutes.

[0042] In certain embodiments of the method of producing an aqueous colloidal silica product, the second intermediate composition is allowed to agitate for 0 minutes to 24 hours, and in certain embodiments for at least 0 minutes, or at least 15 minutes, or at least 30 minutes, up to 24 hours, or up to 18 hours, or up to 12 hours, or up to 6 hours, or up to 3 hours, or up to 2 hours. In certain embodiments of the method of producing the aqueous colloidal silica product, the first or second intermediate products, or both, may be agitated in any one or multiple manners known to the person of skill in the art, including, but not limited to, impeller or paddle mixing, recirculation, air sparging, vibration, vessel shaking, and combinations thereof.

[0043] After 0 minutes to 24 hours of agitation, the first and second portions of aqueous colloidal silica product are separated from the second intermediate composition, thereby producing the aqueous colloidal silica product. In certain embodiments, the separation of the aqueous colloidal silica product from the second intermediate composition is performed using filtration.

[0044] In at least one embodiment, the filtration is performed using another type of liquid/solid separating device constructed and arranged to remove suspended material from a liquid carrier medium. This may be accomplished by any filtration device such as a screen, slotted/perforated pipe, membrane or similar crude filtration device, or combinations thereof. Representative examples include but are not limited to sand filters, filter paper, membrane filters, RO, NF, UF, MF, submerged filters, pressure filters, (centrifuges, cyclones, hydrocyclones, electrostatic precipitators, gravity separators, mist eliminators, screeners, steam traps, absorbers, adsorbers, biofilters, crystalizers, dehumidifiers, distillation columns, dryers, evaporators, extractors, humidifiers, ion exchange columns, strippers), and any combination thereof. In at least one embodiment the filter includes one or more of the filtration techniques disclosed in paper Terminology for Membranes and Membrane Processes, by WJ Koros et al., Journal of Membrane Science, Vol. 120 pp. 149-159 (1996). In at least one embodiment the filter comprises any one or more of the chemical separation processes described on the website: http://encyclopedia.che.engin.umich.edu/Pages/SeparationsChemical/SeparationsChemical.html (as accessed on October 17, 2013) and/or any one or more of the mechanical processes described on the website: http://encyclopedia.che.engin.umich.edu/Pages/SeparationsMechanical/SeparationsMechanical.html (as accessed on October 17, 2013). Membrane filter may be made of polymeric, ceramic, steel or glass materials.

[0045] According to an embodiment, in the method of producing, *e.g.*, aqueous colloidal silica product, the first quantity and the second quantity of alkali metal silicate comprise a total quantity, with the first quantity ranging from 60 to 95 weight percent, or 65 to 90 weight percent, or 70 to 80 weight percent, of the total quantity, and in certain embodiments being at least 60 weight percent, or at least 65 weight percent, or at least 70 weight percent, up to 95 weight percent, or up to 90 weight percent, or up to 85 weight percent or up to 80 weight percent, or up to 75 weight percent of the total quantity.

[0046] Generally, the alkali metal silicate (both the first and second quantities thereof) that is added in the method of the second exemplary embodiment is selected from the group consisting of sodium silicate, potassium silicate, lithium silicate and combinations thereof. In certain embodiments, the alkali metal silicate is sodium silicate. While the first and second quantities of alkali metal silicate are generally the same composition (*e.g.*, generally having the same chemical composition, same physical properties, same impurities, etc.), the first and second quantities can in theory be compositions having differing physical or chemical characteristics. For example, the first quantity is sodium silicate and the second quantity is potassium silicate. In certain embodiments, the first and second quantities of the alkali metal silicate are the same composition. For example, the first quantity is sodium silicate and the second quantity is the same type of sodium silicate.

[0047] While the quality of the starting ingredients (*i.e.*, alkali metal silicate, cationic ion exchange resin, water, etc.) may provide some variation in the aqueous colloidal silica product, the method has unexpectedly produced aqueous colloidal silica product having properties particularly beneficial to the papermaking industry, for example as retention and dewatering aids. The alkali metal silicate can be any number of conventional materials, such as water glasses. The mole ratio of SiO_2 to Na_2O, or K_2O, or Li_2O, or combination of Na_2O, K_2O and Li_2O, in the alkali metal silicate, can be in the range from 15:1 to 1:1 and is preferably within the range from 2.5:1 to 3.9:1. Such alkali metal silicate solution typically will have a pH in excess of 10, typically at least 11. Such alkali metal may contain impurities, include but not limited to aluminum, iron, calcium, magnesium, chloride, and sulfate ions. The solids contains in the said alkali metal silicate can in the range from about 15 to 40 percent by weight as SiO_2.

[0048] The water used in producing the aqueous colloidal silica product is not particularly limited and may be any reasonably soft fresh water (*i.e.*, not brine and having less than 2000 μS/cm conductance). In certain embodiments, the water is tap water, well water, distilled water, deionized water, otherwise purified water, or any combination thereof.

[0049] The cationic ion exchange resin utilized in the methods of the second exemplary embodiment is not particularly limited. In certain embodiments, the cationic ion exchange resin is preferable to be a weak acid cationic resin, includes but not limited to, Amberlite® IRC84SP.

[0050] In certain embodiments, the cationic ion exchange resin may be reused from previous production processes after regeneration. The cationic ion exchange resin may be regenerated using an organic or mineral acid. Exemplary embodiments of acids that may be used to regenerate the cationic ion exchange resin include, but are not limited to, the following: sulfuric acid, hydrochloric acid, phosphoric acid, or such materials as carbon dioxide, and combinations thereof. Examples of suitable organic acids include but are not limited to: acetic acid, formic acid and propionic acid. In certain embodiments, mineral and organic salts may be used as a weak acid to regenerate the resin or be used to reduce the colloidal silica product viscosity. Example of suitable salts includes but not limited to: sodium sulfate, sodium acetate, potassium sulfate, potassium acetate, trisodium phosphate and sodium monohydrogen phosphate.

[0051] While the cationic ion exchange resin has an ion exchange capacity in the hydrogen form that is not particularly limited, in certain embodiments, the cationic ion exchange resin has an ion exchange capacity of 40 to 100%, or 50 to 100% or 60 to 100%, and in certain embodiments at least 40%, or at least 50%, or at least 60%, in the hydrogen form.

[0052] Unexpectedly, methods according to the second embodiment have been shown to be capable of producing an aqueous colloidal silica product having from 16 to 18 weight percent colloidal silica solids, a viscosity ranging from 4 to 20 cps, an S-value ranging from 26 to 40%, and with colloidal silica solids having a specific surface area ranging from 700 to 850 m^2/g, all without using silicic acid or ultrafiltration.

[0053] In certain embodiments of the second exemplary embodiment, the first or second intermediate composition, the aqueous colloidal silica product, or any, or all of the aforementioned have a pH ranging from 8 to 11, and the pH may further range from 9 to 11.

[0054] In certain embodiments of the second exemplary embodiment, the first and second intermediate compositions have temperatures ranging from 100 to 160 degrees Fahrenheit.

[0055] In certain embodiments of the second exemplary embodiment, the first rate of adding the alkali metal silicate is sufficient to allow the addition of the first quantity of alkali metal silicate to last from 1 to 45 minutes. In certain embodiments of the second exemplary embodiment, the second rate of adding the alkali metal silicate is sufficient to allow the addition of the second quantity of alkali metal silicate to last from 5 to 120 minutes.

[0056] The aqueous colloidal silica product described herein may be used in any one or more of several manufacturing processes, including, but not limited to, the following: papermaking processes, for example, retention and drainage, pulp dewatering; water treatment and wastewater treatment processes, for example sludge dewatering, clarification and dewatering of aqueous mineral slurries, refinery emulsion breaking and the like; food and beverage processes, for example, for beer, wine, juice, and sugar clarification. The aqueous colloidal silica product described herein is particularly suited for use in the papermaking process.

[0057] The method may be used according to any one, some, or all, of the methods and processes for utilizing colloidal silica as described in the *Handbook for Pulp and Paper Technologists*, by Gary A. Smook, Angus Wilde Publicatiosn Inc., (2001). In addition, the aqueous colloidal silica product can be added to a cellulosic furnish at the wet end of the papermaking process, thereby enhancing the retention of filler ("ash") in the cellulosic furnish, and consequently in the cellulosic sheet, while further aiding in the drainage of water from the cellulosic furnish.

[0058] At least one embodiment of the present disclosure is directed to a method of making a cellulosic sheet. The method comprises preparing a cellulosic furnish containing from 0.01 to 1.5 weight percent cellulosic fiber based upon the total weight of the cellulosic furnish (*i.e.*, including water). An amount of an aqueous colloidal silica product as described herein, and an amount of a water soluble polymeric flocculant, is added to the cellulosic furnish. The amount of the aqueous colloidal silica product added to the cellulosic furnish is sufficient to achieve a concentration of colloidal silica solids of from about 0.00005 to about 1.5 weight percent per dry weight of fiber in the cellulosic furnish. In other words, for every 100 lbs of fiber (dry weight) in the cellulosic furnish, 0.00005 to 1.5 lbs of colloidal silica solids will be present. The amount of the water soluble polymeric flocculant added to the cellulosic furnish is sufficient to achieve a concentration of water soluble polymeric flocculant of from about 0.001 to about 5 weight percent per dry weight of fiber in the cellulosic furnish. The water soluble polymeric flocculant has a molecular weight ranging from 500,000 to 30 million daltons. The cellulosic furnish is then dewatered in a fashion known by those of skill in the art to thereby obtain a cellulosic sheet. A cationic starch may alternatively be added to the furnish in place of, or in addition to the synthetic polymer flocculant in an amount of from about 0.005 to about 5.0 percent by weight based on the dry weight of fiber in furnish. More preferably, the starch is added in an amount of from about 0.5 to about 1.5 percent by weight based on the dry weight of fiber in the furnish. In yet another embodiment, a coagulant may be added to the furnish in place of, or in addition to, the flocculant and/or the starch in an amount of from about 0.005 to about 1.25 percent by weight based on the dry weight of fiber in the papermaking furnish. Preferably, the coagulant is added in an amount of from about 0.025 to about 0.5 percent by weight based on the dry weight of fiber in the furnish.

[0059] In certain embodiments of the method of making the cellulosic sheet, the aqueous colloidal silica product is added to the cellulosic furnish.

[0060] Non-limiting examples of water soluble polymeric flocculants suitable for use in certain embodiments according to the third exemplary embodiment include cationic, anionic, amphoteric, and zwitterionic polymers. Examples of cationic water soluble polymer flocculants include cationized starch, and homopolymers and copolymers comprising the following monomers: dimethylaminoethyl methacrylate ("DMAEM"), dimethylaminoethyl acrylate ("DMAEA"), diethylaminoethyl acrylate ("DEAEA"), diethylaminoethyl methacrylate ("DEAEM"), or their quaternary ammonium forms made with dimethyl sulfate or methyl chloride; mannich reaction modified polyacrylamides; diallylcyclohexylamine hydrochloride ("DACHA HCl"); diallyldimethylammonium chloride ("DADMAC"); methacrylamidopropyltrimethylammonium chloride ("MAPTAC"); and allyl amine ("ALA").

[0061] In certain embodiments, the amount of the aqueous colloidal silica product added to the cellulosic furnish is sufficient to achieve a colloidal silica solids concentration of 0.00005 to 1.5 weight percent, or 0.0005 to 1 weight percent, or 0.005 to 0.05 weight percent, per dry weight of fiber in the cellulosic furnish, and in certain embodiments from at least 0.00005, or at least 0.0005, or at least 0.005, or at least 0.05, up to 0.5, or up to 1, or up to 1.5 weight percent per dry weight of fiber in the cellulosic furnish.

[0062] First pass ash retention ("first pass ash retention" or "FPAR") is a parameter that is important to papermakers when determining filler retention in the cellulosic furnish, and consequently in the cellulosic sheet. Aqueous colloidal silica product added to the cellulosic furnish allows for increased first pass ash retention, while not detrimentally affecting the water drainage from the cellulosic furnish. In fact, the aqueous colloidal silica product of the present disclosure has been found to aid in water drainage from the cellulosic furnish.

[0063] Furthermore, the first pass ash retention can be used to calculate a first pass ash retention replacement ratio, which is a ratio of the amount of microparticle dose needed to achieve an equivalent first pass ash retention when utilizing the aqueous colloidal silica product of the present disclosure as compared to when utilizing an aqueous colloidal silica product produced using the batch process known in the art (such as US Patents 6,372,089 and 6,372,806). The first pass ash retention replacement ratio is illustrated in Equation 1 below:

[0064]

$$\begin{aligned} &FPAR\ Replacement\ Ratio \\ &= \frac{Microparticle\ Dose\ for\ Cellulosic\ Sheet\ Utilizing\ Inventive\ AqCSP\ to\ achieve\ x\ FPAR}{Microparticle\ Dose\ for\ Cellulosic\ Sheet\ Utilizing\ Batch\ AqCSP\ to\ achieve\ x\ FPAR} \end{aligned} \qquad (1)$$

[0065] As can be deduced from Equation 1 and as illustrated in FIG. 1, improvement in the first pass ash retention is shown when the FPAR replacement ratio is less than one. For cellulosic sheets utilizing a “batch” aqueous colloidal silica product and achieving a first pass ash retention of 90%, the microparticle dose required to achieve the 90% FPAR is approximately 1.6 lb of microparticles per ton of cellulosic furnish, based on dry cellulosic fibers. In certain embodiments, cellulosic sheets incorporating the aqueous colloidal silica product of the present disclosure, and at the same colloidal silica solids amount per dry weight of fiber, has been shown to be capable of achieving a 90% FPAR at about 0.9 to about 1.2 lb of microparticles per ton dry weight of fiber in the cellulosic furnish. Thus, in certain embodiments, the FPAR replacement ratio for a cellulosic sheet incorporating the inventive aqueous colloidal silica product ranges from about 0.5 to about 0.8.

EXAMPLES

[0066] The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the invention. In particular the examples demonstrate representative examples of principles innate to the invention and these principles are not strictly limited to the specific condition recited in these examples. As a result it should be understood that the invention encompasses various changes and modifications to the examples described herein and such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

Example 1:

[0067] Preparation of a Colloidal Silica Sol of the Invention. Inventive aqueous colloidal silica products (Samples 7-15 in Table 1) were prepared using the lab-scale semi-batch procedure described as follows. Charge a reaction vessel with 600 mL of Amberlite® IRC84SP ion exchange resin (available from Dow) in its sodium form. Following manufacturer's procedure for regenerating the resin to the hydrogen form such that the regeneration is at least 40 percent complete. Rinse the resin clean with water and drain the water. Charge 190-380 grams of water into the vessel and start mixing the contents of the vessel to suspend the resin. Next, heat the contents of the reactor to 100-160 degrees F. Charge the reaction vessel (over a period of about 2-20 minutes) with 186-505 grams of sodium silicate (having a mole ratio of SiO_2 to Na_2O of 3.26 and a pH of 11.2). After 1-45 min, charge the reaction vessel (over a period of about 5-30 minutes) with 13-160 grams of sodium silicate. Stir the contents in the reaction vessel for another 10-180 minutes. Then, remove the contents from the reaction vessel and separate the colloidal silica product from ion exchange resin via a filter bag.

[0068] Preparation of a Colloidal Silica Sol using conventional batch process. For comparative samples produced using the batch method (Sample 1-6). Charge a reaction vessel with 600 mL of Amberlite® IRC84SP ion exchange resin (available from Dow) in its sodium form. Following manufacturer's procedure for regenerating the resin to the hydrogen form such that the regeneration is at least 40 percent complete. Rinse the resin clean with water and drain the water. Charge 190-380 grams of water into the vessel and start mixing the contents of the vessel to suspend the resin. Next, heat the contents of the reactor to 100-160 degrees F. Charge the reaction vessel (over a period of about 2-20 minutes) with 266-532 grams of sodium silicate (having a mole ratio of SiO_2 to Na_2O of 3.26 and a pH of 11.2). Stir the contents in the reaction vessel for another 10-180 minutes. Then, remove the contents from the reaction vessel and separate the colloidal silica product from ion exchange resin via a filter bag.

Table 1. Lab-scale Samples Prepared via Batch Method (Samples 1–6) or Inventive Semi-batch Method (Samples 7–15)

Sample	SiO_2 Addition, Batch ("B") or Semi-batch ("S")	Colloidal Silica Solids concentration (wt %)	pH	Viscosity (cP)	Conductivity, μS/cm	Specific Surface Area (m^2/g)	S-value (%)
1	B	16.02	10.26	41.2	5560	831	25.8
2	B	16.37	10.46	22.2	6610	850	27.2
3	B	16.05	11.13	50	10260	870	18.9
4	B	16.49	10.78	25	6870	869	26.5
5	B	16.68	10.14	25	6710	888	27.9
6	B	17.07	n/a	58	n/a	n/a	28.0
7	S	16.80	10.48	5.46	7210	832	33.1
8	S	16.5	10.22	10.3	6400	836	33.1
9	S	16.4	10.11	13.2	5330	719	32.6
10	S	16.4	10.39	9.2	6180	770	30.7
12	S	17.2	10.24	15.6	6700	836	29.6
13	S	16.5	9.9	16.5	5820	777	32.6
14	S	16.7	9.9	13.8	5810	789	34.8
15	S	17.1	10.21	11.4	6500	846	33.0

[0069] As can be seen from Table 1, the samples prepared by the conventional batch method that achieve at least 16% colloidal silica solids (e.g., Samples 1-6) all fail to meet the claimed upper limit related to viscosity. However, Samples 7–15, prepared using the semi-batch method outlined herein, all unexpectedly achieved 16–18 weight percent colloidal silica solids while meeting the claim limitations recited for viscosity (4–20 cP), S-value (26–35%), and specific surface area of the colloidal silica solids (700–850 m^2/g).

Example 2:

[0070] For Example 2, inventive aqueous colloidal silica products (Samples 16-29 in Table 2) were prepared using the following pilot-scale semi-batch procedure.

Charge a reaction vessel with 185 gallons of Amberlite® IRC84SP ion exchange resin (available from Dow) in its sodium form. Following manufacturer's procedure for regenerating the resin to the hydrogen form such that the regeneration is at least 40 percent complete. Rinse the resin clean with water and drain the water. Charge 683-1158 lbs of water into the vessel and start mixing the contents of the vessel to suspend the resin. Next, heat the contents of the reactor to 100-160 degrees F. Charge the reaction vessel (over a period of about 2-20 minutes) with 574-1320 lbs of sodium silicate (having a mole ratio of SiO_2 to Na_2O of 3.26 and a pH of 11.2). After 1-45 min, charge the reaction vessel (over a period of about 5-30 minutes) with 41-417 lbs of sodium silicate. Stir the contents in the reaction vessel for another 10-180 minutes. Then, remove the contents from the reaction vessel from the bottom through the screen.

Table 2: Pilot-scale Samples Prepared via Inventive Semi-batch Method

Sample	Colloidal Silica Solids concentration (wt %)	pH	Viscosity (cP)	Specific Surface Area (m^2/g)	S-value (%)
16	17.8	10.7	11	766	34.0
17	17.3	10.6	14	773	30.9
18	17.3	10.6	15	720	33.0
19	16.7	10.7	11	773	29.7
20	17.4	10.7	11	762	35.0
21	17.1	10.6	20	788	30.0
22	17.4	10.7	18	801	27.0
23	17.1	10.7	20	793	29.0
24	17.2	10.8	12	812	32.0
25	17.0	10.6	9	758	34.0
26	17.1	10.7	10	780	33.4
27	17.2	10.7	13	777	31.1
28	16.8	10.7	9	782	33.6
29	16.9	10.6	11	785	33.0

[0071] As can be seen from Table 2, each of the pilot-scale samples achieved the claimed parameters even with colloidal silica solids as high as about 18% (Sample 16).

Example 3:

[0072] A control sample and Samples 17-19 of Example 2 were utilized in comparison experiments related to first pass ash retention of each. Each of the samples were dosed onto a cellulosic furnish.

[0073] As can be seen, a 90% first pass ash retention can be achieved using approximately 0.5 to 0.8 as much microparticle dosage (FPAR replacement ratio) for each of Samples 17–19, as compared to the control sample. These results are graphically demonstrated in FIG. 1.

	First Pass Ash Retention (%)				
Microparticle Dosage, lb microparicles/ton	Control	Sample 17	Sample 18	Sample 19	
0	73.5	73.5	73.5	73.5	
0.25	79.2	76.3	76.7	79.1	
0.5	80.5	82.7	83.0	84.0	
1	85.5	90.4	88.2	90.4	
1.5	89.3	95.1	94.9	94.6	
2	92.2	94.8	94.9	96.9	

[0074] As can be seen, the inventive aqueous colloidal silica products prepared using the inventive production method provided superior results compared to the control sample.

[0075] To the extent that the terms “include,” “includes,” or “including” are used in the specification or the claims, they are intended to be inclusive in a manner similar to the term “comprising” as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term “or” is employed (*e.g.*, A or B), it is intended to mean “A or B or both A and B.” When the applicants intend to indicate “only A or B but not both,” then the term “only A or B but not both” will be employed. Thus, use of the term "or" herein is the inclusive, and not the exclusive use. Also, to the extent that the terms "in" or "into" are used in the specification or the claims, it is intended to additionally mean "on" or "onto."

[0076] The general inventive concepts have been illustrated, at least in part, by describing various exemplary embodiments thereof. While these exemplary embodiments have been described in considerable detail, it is not the Applicant's intent to restrict or in any way limit the scope of the appended claims to such detail. Furthermore, the various inventive concepts may be utilized in combination with one another *(e.g.,* one or more of the first, second, third, fourth, etc., exemplary embodiments may be utilized in combination with each other). Additionally, any particular element recited as relating to a particularly disclosed embodiment should be interpreted as available for use with all disclosed embodiments, unless incorporation of the particular element would be contradictory to the express terms of the embodiment. Additional advantages and modifications will be readily apparent to those skilled in the art. Therefore, the disclosure, in its broader aspects, is not limited to the specific details presented therein, the representative apparatus, or the illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the general inventive concepts.

[0077] The invention encompasses any possible combination of some or all of the various embodiments mentioned and/or described herein. In addition, the invention encompasses any possible combination that also specifically excludes any one or some of the various embodiments mentioned and/or described herein.

CLAIMS:

1. An aqueous colloidal silica product comprising water and from 16 to 18 weight percent colloidal silica solids, wherein the aqueous colloidal silica product has a viscosity ranging from 4 to 20 cps and an S-value ranging from 26 to 40%, wherein the colloidal silica solids have a specific surface arca ranging from 750 to 850 m^2/g.

2. The aqueous colloidal silica product of claim 1, further comprising an alkali metal.

3. The aqueous colloidal silica product of claim 2, wherein the alkali metal is present in an amount sufficient to provide a molar ratio of silica to alkali metal ranging from 50:1 to 5:1.

4. The aqueous colloidal silica product of any one of claims 1-3, wherein the aqueous colloidal silica product has a viscosity ranging from 4 to 18 cps.

5. The aqueous colloidal silica product of any one of claims 1-4, wherein the aqueous colloidal silica product comprises from 17 to 18 weight percent colloidal silica solids.

6. The aqueous colloidal silica product of any one of claims 1-3, wherein the aqueous colloidal silica product has a ratio of weight percent colloidal silica solids to cps viscosity ranging from 1:2 to 4:1.

7. The aqueous colloidal silica product of any one of claims 1-6, wherein the aqueous colloidal silica product has a pH ranging from 9 to 11.

8. The aqueous colloidal silica product of any one of claims 1-6, wherein the aqueous colloidal silica product has a pH ranging from 10 to 11.

9. A method of making a cellulosic sheet, the method comprising:

preparing a cellulosic furnish containing from 0.01 to 1.5 weight percent cellulosic fiber;

adding to the cellulosic furnish an amount of the aqueous colloidal silica product of claim 1 sufficient to achieve a concentration of colloidal silica solids of from 0.00005 to 1.5 weight percent per dry weight of fiber in the cellulosic furnish, and an amount of a water soluble polymeric flocculant sufficient to achieve a concentration of water soluble polymeric flocculant of from 0.001 to 5 weight percent per dry weight of fiber in the cellulosic furnish, wherein the water soluble polymeric flocculant has a molecular weight ranging from 500,000 to 30 million daltons; and

dewatering the cellulosic furnish to obtain the cellulosic sheet.

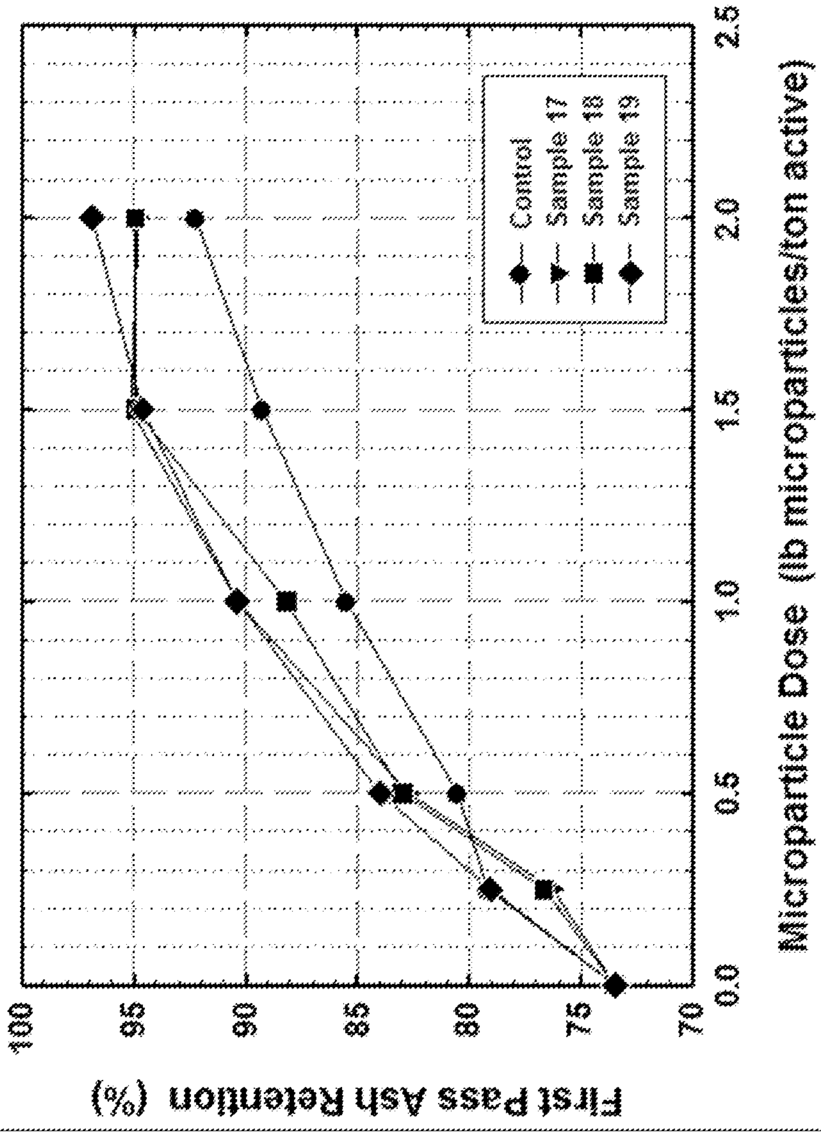
10. The method of claim 9, wherein the amount of the aqueous colloidal silica product added to the cellulosic furnish is sufficient to achieve a colloidal silica solids concentration of from 0.005 to 1 weight percent per dry weight of fiber in the cellulosic furnish.

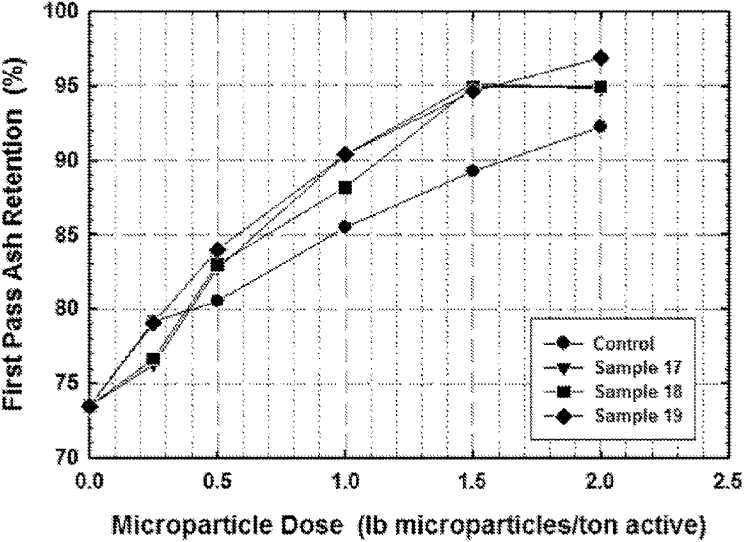
11. The method of claim 9 or 10, wherein the colloidal silica product has a first pass ash retention replacement ratio ranging from 0.5 to 0.8 relative to a batch aqueous colloidal silica product.

12. The method of claim 9 or 10, wherein the colloidal silica product achieves a first pass ash retention of at least 90% relative to a batch aqueous colloidal silica product when dosing microparticles into the cellulosic furnish at a concentration of 0.41 to 0.54 kilograms per 907 kilograms of dry weight of fiber in the cellulosic furnish.

13. The method of any one of claims 9-12, wherein a cationic starch is added to the cellulosic furnish in an amount sufficient to achieve a concentration of cationic starch of from 0.005 to 5 weight percent cationic starch per dry weight of fiber in the cellulosic furnish.

FIG. 1


First Pass Ash Retention (%)
100
95
90
85
80
75
70
0.0
0.5
1.0
1.5
2.0
2.5
Microparticle Dose (lb microparticles/ton active)
Control
Sample 17
Sample 18
Sample 19


First Pass Ash Retention (%)
100
95
90
85
80
75
70
0.0
0.5
1.0
1.5
2.0
2.5
Microparticle Dose (lb microparticles/ton active)
Control
Sample 17
Sample 18
Sample 19