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(54) **ENHANCED BULK AND HIGH STRENGTH PAPER**

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(57)

**ABSTRACT**

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**Related U.S. Application Data**

(63) Continuation of application No. PCT/US2013/076653, filed on Dec. 19, 2013.

(60) Provisional application No. 61/745,725, filed on Dec. 24, 2012, provisional application No. 61/774,295, filed on Mar. 7, 2013.

**Publication Classification**

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Disclosed herein are systems and methods for attaching particulate additives to a population of cellulose fibers dispersed in an aqueous solution. The cellulose fibers are treated with an activator that forms complexes with them. The particulate additive is attached to a tether that is capable of interacting with the activator, thereby forming a tether-bearing particulate additive. The tether-bearing particulate additive can be added to the activated suspension of cellulose fibers. The resulting interaction between the tether and the activator forms durable complexes that attach the particulate additive to the cellulose fibers. Using these systems and methods, useful additives like starches can be attached to cellulose fibers, imparting advantageous properties such as increased strength to paper products formed thereby. These systems and methods are particularly useful for papermaking involving virgin pulp fibers, recycled fibers, or any combination thereof.

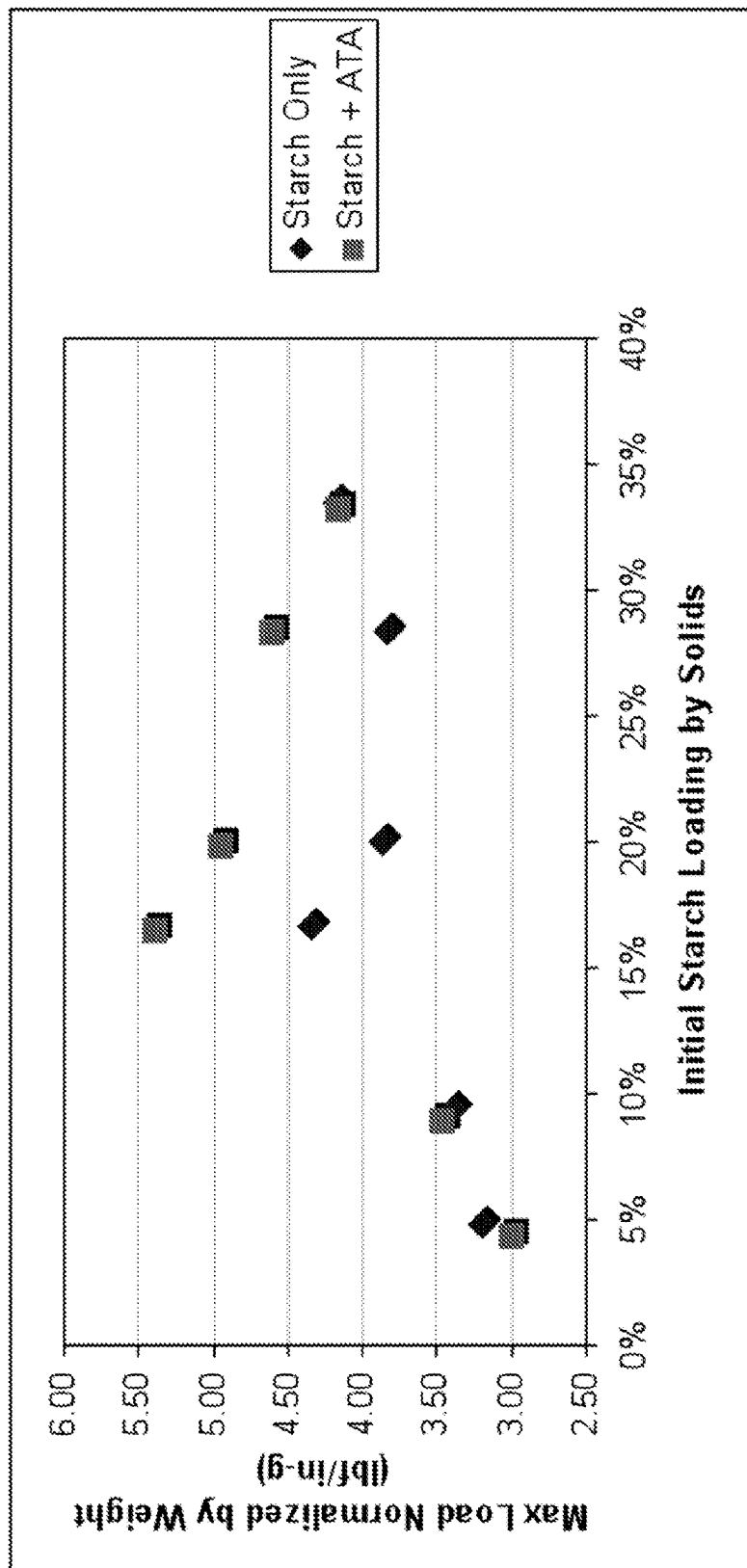


FIG. 1

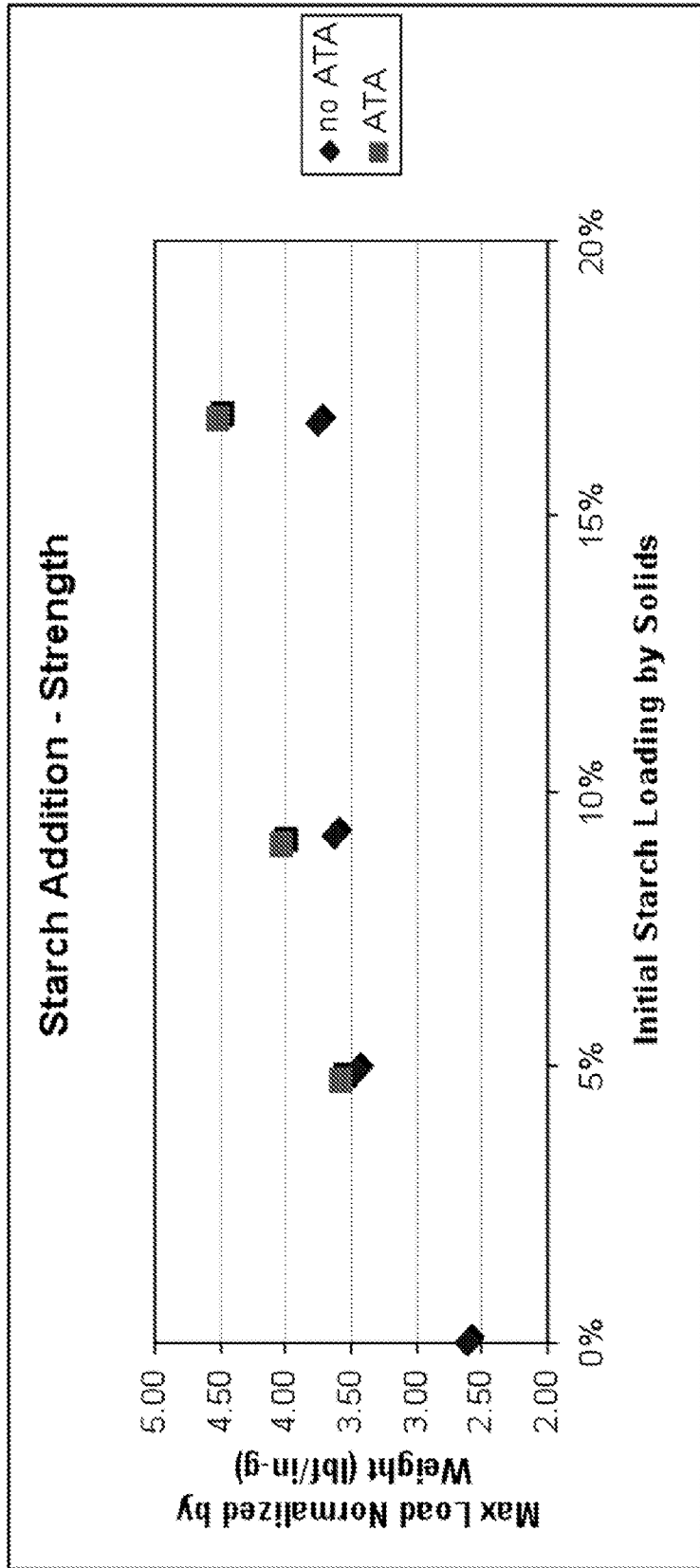


FIG. 2

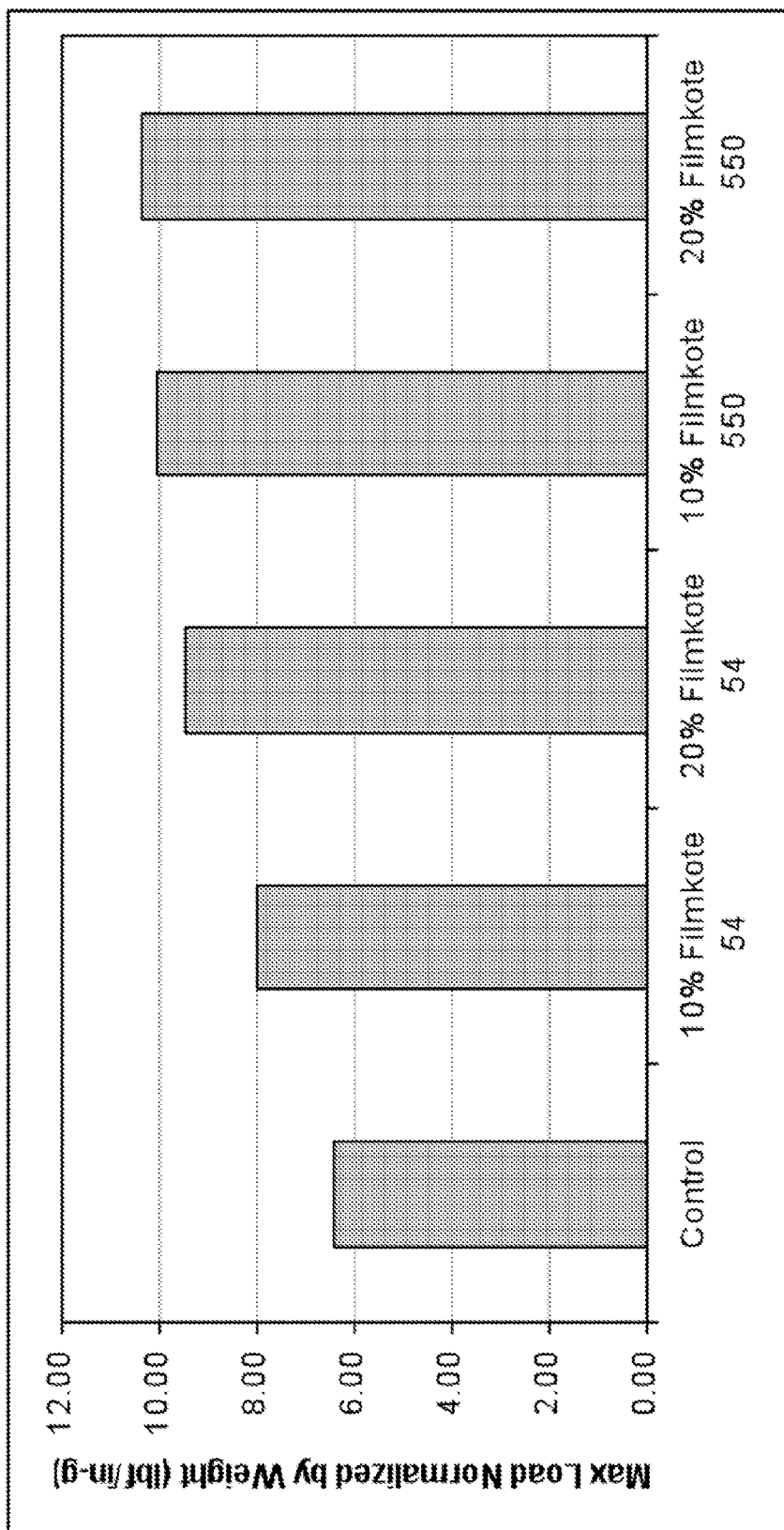


FIG. 3

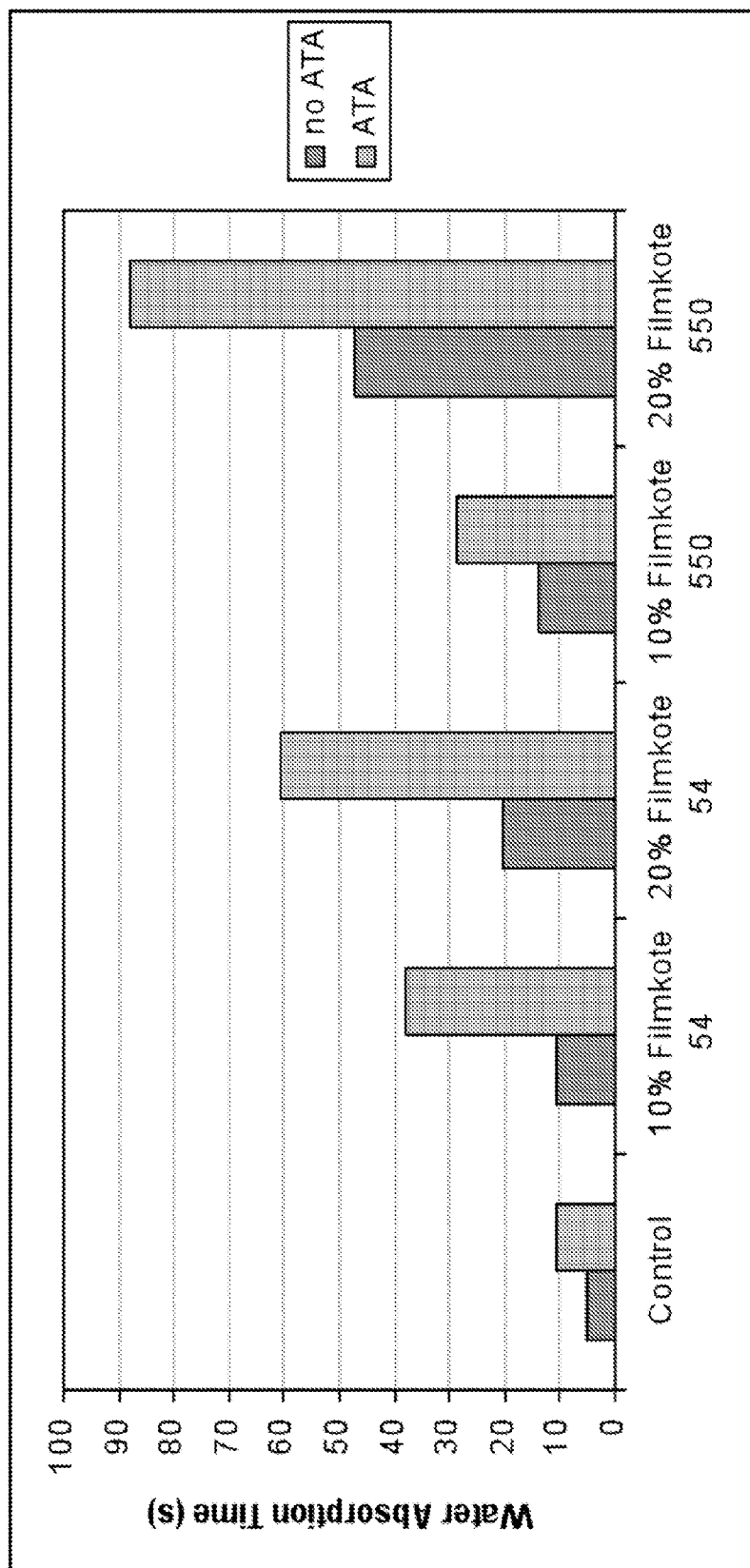


FIG. 4

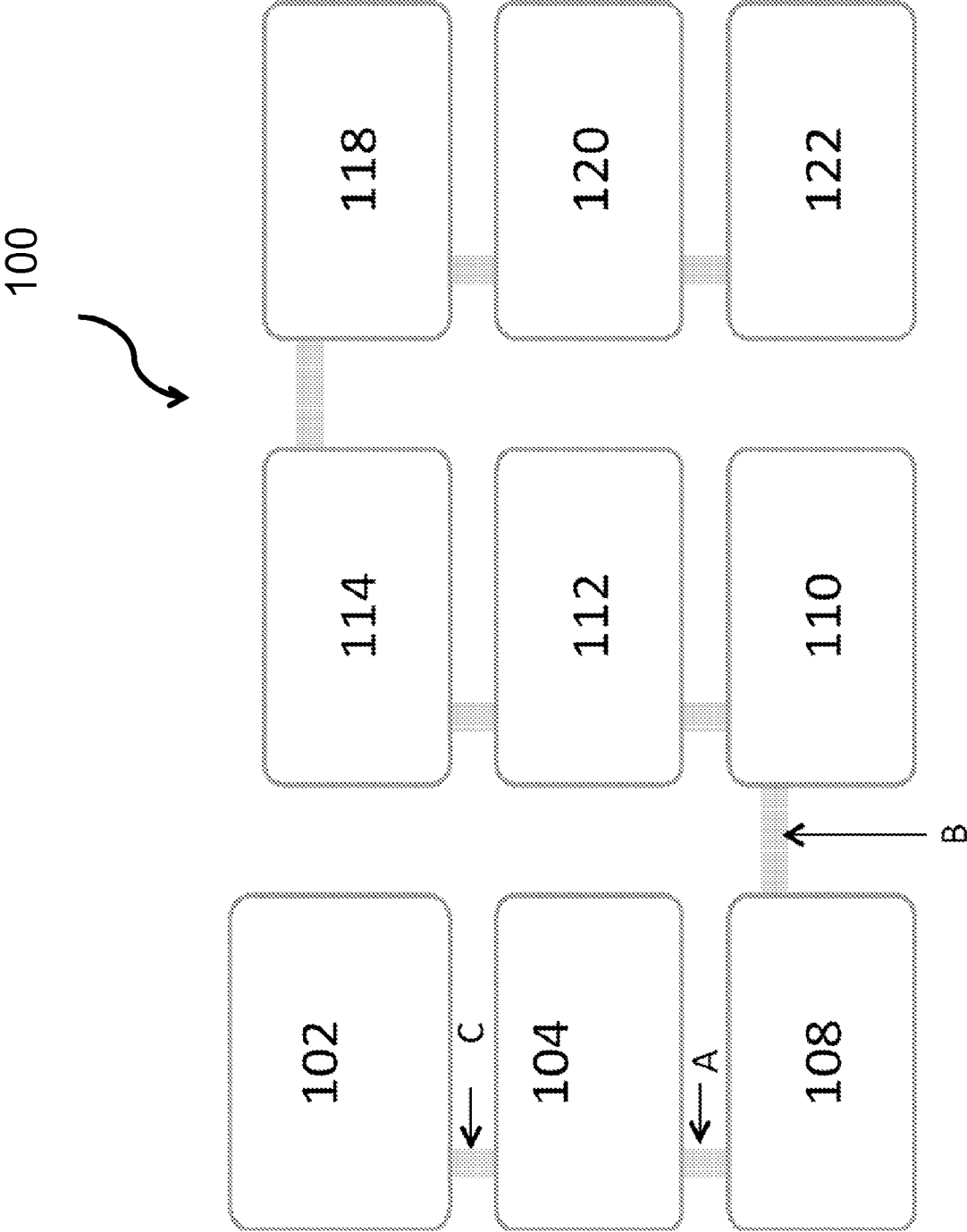


FIG. 5

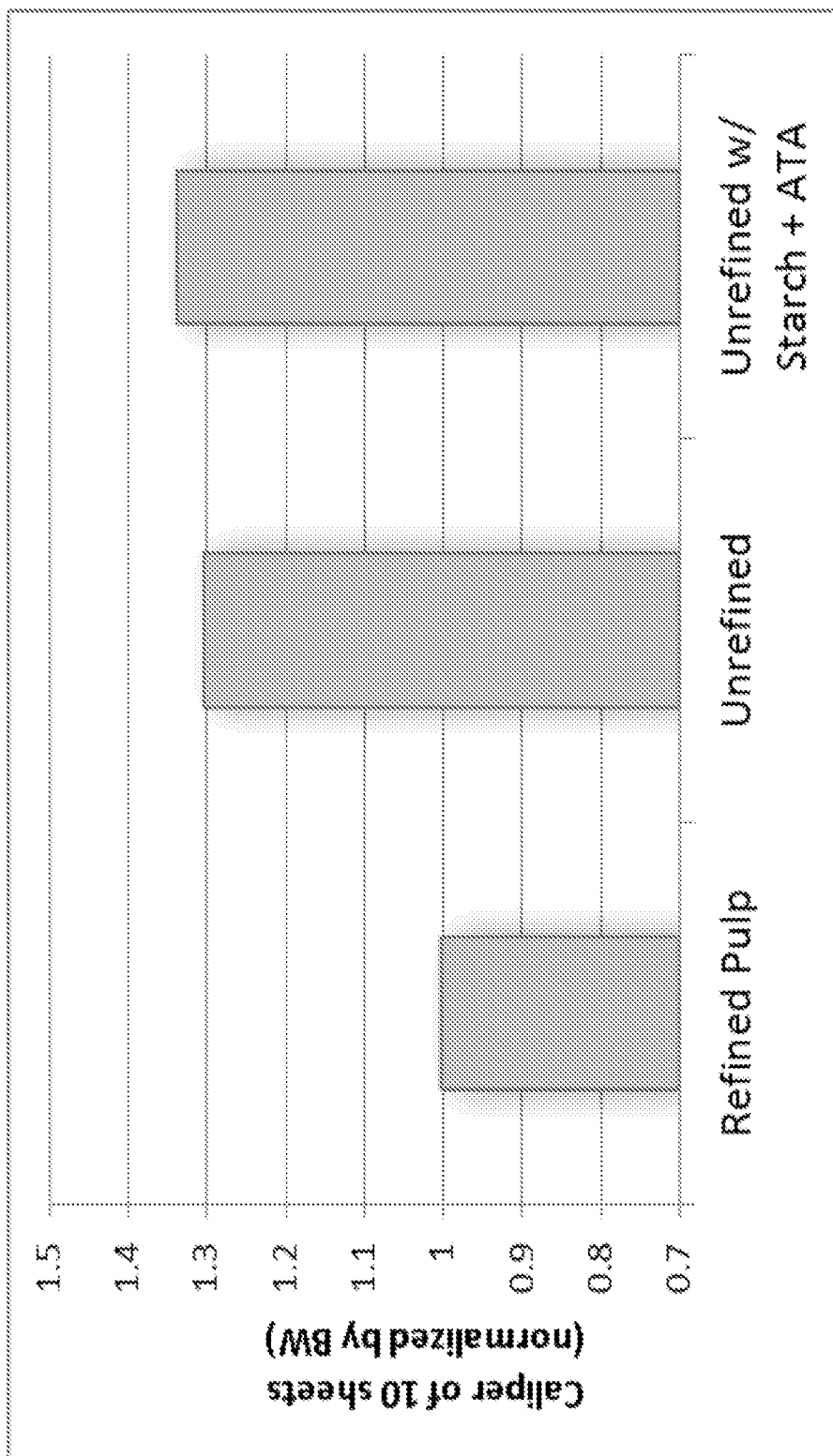


FIG. 6

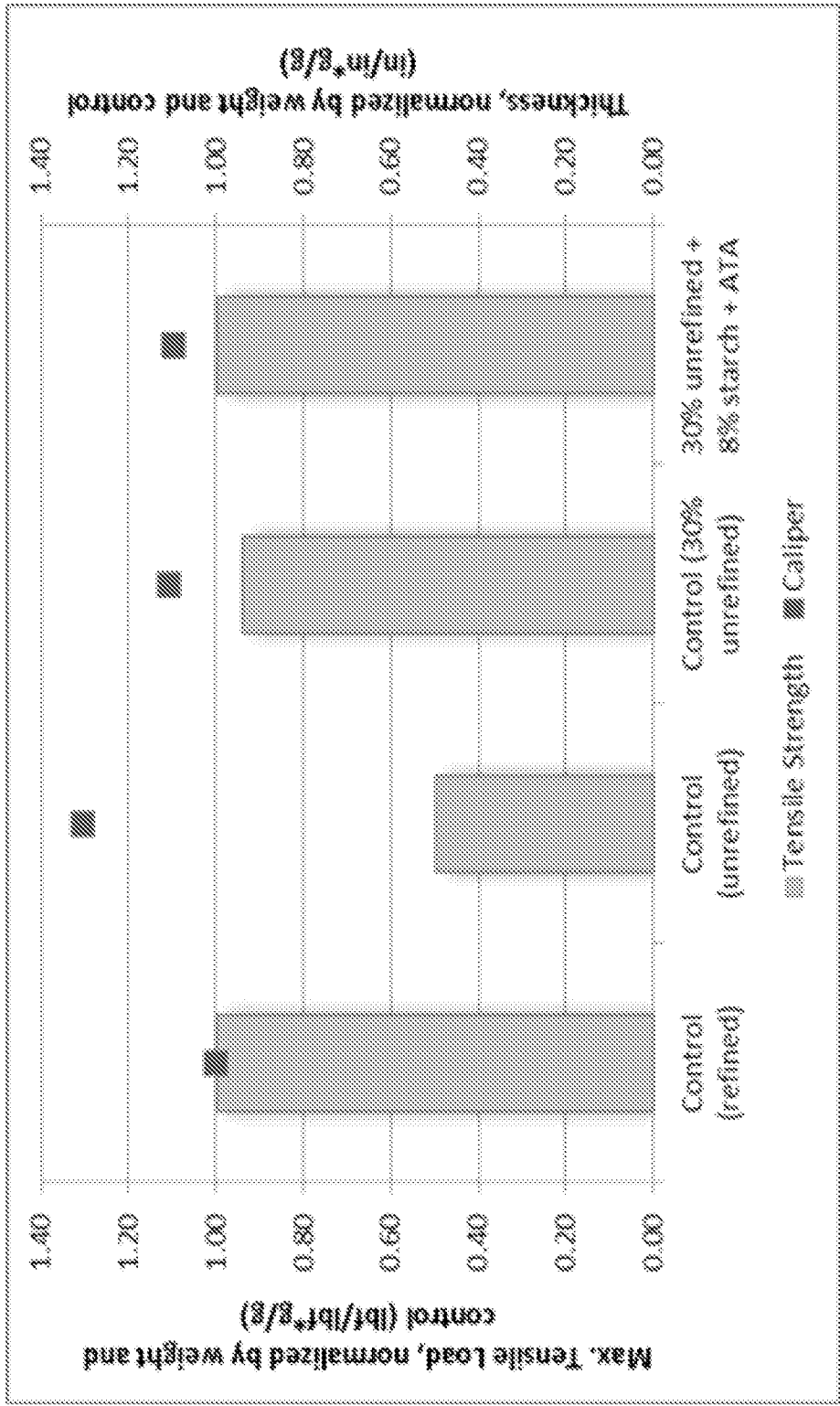


FIG. 7

## ENHANCED BULK AND HIGH STRENGTH PAPER

### RELATED APPLICATIONS

[0001] This application is a continuation of International Application No. PCT/US2013/076653, which designated the United States and was filed on Dec. 19, 2013, published in English, which claims the benefit of U.S. Provisional Application Ser. No. 61/745,725, filed on Dec. 24, 2012 and U.S. Provisional Application Ser. No. 61/774,295 filed Mar. 7, 2013. The entire contents of the above applications are incorporated by reference herein.

### FIELD OF THE APPLICATION

[0002] This application relates generally to making paper products.

### BACKGROUND

[0003] High bulk is desirable in many paper and paperboard applications. High bulk is beneficial when same or higher thickness can be achieved by using the same amount of pulp (same basis weight). This is useful particularly in packaging applications where the stiffness of the packaging board is directly proportional to the cube of the thickness of the board. Thus doubling of the bulk or thickness of the board at same weight would increase the stiffness by a factor of eight. Many approaches have been used in the past towards achieving high bulk. Use of debonding molecules that decrease the hydrogen bonding between fibers increase bulk, as does the use of expandable particles. Debonders make the paper weak, however, while expandable particles are expensive and fragile.

[0004] Traditionally, the fibers that are used in paper making are refined to increase fiber-fiber contact, thereby increasing the strength of the paper. This is done particularly when softwood (long fibers) and hardwood (stiff short fibers) are mixed to produce paper or paperboard. Hardwood is cheaper than softwood and usually is the predominant fiber in paper because of price and density. The somewhat cylindrical softwood fibers are often refined (i.e., subjected to high shear) to produce flat ribbon-like fibers that have fibrillated surfaces to improve interfiber contacts and bonding among themselves and with the shorter hardwood fibers. Refined fibers also have improved surface properties that allow for a smoother surfaced with decreased pore size. Refining also reduces the bulk of a paper matrix by turning a round reed-like fiber into a flat, ribbon-like structure. These flat fibers attach well to other fibers, yielding dense and strong sheets at the expense of bulk. If unrefined fibers are used in an effort to produce a bulkier paper product, the resulting sheet can be weak and even unusable.

[0005] High strength is desirable in many paper and paperboard applications, however, and there are many ways to achieve it. One way to achieve this is by manufacturing dense, high-caliper sheets or boards. This requires the use of large amounts of expensive pulp, and produces a heavy product. Another method of creating high strength in paper products is to add starch as sizing.

[0006] In one approach, the sizing process uses cooked starch solutions to impart stiffness or strength to the paper. In the sizing process, the wet web is first dried to a pre-set moisture content and/or is re-wet to achieve uniform moisture content throughout; then the material is fed into a size press

where a high loading of gelatinized starch is applied to the paper surface; then the material is dried again. This process yields a strong paper, but involves a number of downstream processes that can be inefficient. Inefficiencies result from the number of steps involved in preparing the substrate, cooking the starch and applying it to form the finished product. A considerable amount of energy is required for these steps, which adds to the costs of the process.

[0007] In some instances, gelatinized starch can be added to the wet end of the papermaking process, but its retention on the pulp fibers is often poor. Such starch granules can gelatinize during the drying process, imparting stiffness and strength to the paper web once it is dry. Adding starch granules in this manner requires lower amounts of energy to dry the paper web, while also eliminating or reducing the use of a size press. Moreover, the contamination of the whitewater with gelatinized starch leads to increased biological oxygen demand of the effluent, so that the process is environmentally unfavorable.

[0008] Starch as a bonding agent between the fibers can also be incorporated in the form of ungelatinized starch granules. Ungelatinized starch granules can be added to the wet end of papermaking, but they are poorly retained. Such starch granules can gelatinize during the drying process, imparting strength to the paper web once it is dry. Adding starch granules in this manner requires lower amounts of energy to dry the paper web, while also eliminating or reducing the use of a size press. As an alternative, ungelatinized starch granules can be incorporated as fillers. In their native state, ungelatinized starch granules do not absorb water like the gelatinized starches, so they can be applied to paper webs that have not been pre-dried. Moreover, the granules once incorporated in the fiber matrix, gelatinize locally thereby acting as internal bonding between fiber joints without adequately impacting the bulking of the paper. To apply ungelatinized starch, these granules can be sprayed on the moving moist web, and gelatinization can be effected in the dryer. This yields an improvement in dry strength and stiffness of the paper. However, the spraying process does not disperse starch uniformly throughout the thickness of the paper, leading to anisotropic stiffness and strength properties.

[0009] There remains a need in the art, therefore, for systems and methods for incorporating and retaining ungelatinized starch fillers in the wet end so that high amounts of these fillers are dispersed uniformly in the paper. These fillers should, desirably, be incorporated so that they are stably anchored to the pulp fibers, allowing them to expand or gelatinize during paper manufacturing without being dislodged. In this manner, the fillers can occupy the interstitial spaces between cellulose fibers more completely, improving the rigidity of the paper product. Furthermore, it is known that high filler content has a detrimental effect on the strength of the wet web before it is dried because the fillers act as spacers and interfere with fiber-fiber bonding. An efficient retention system that attaches the fillers to fibers durably in the wet web can advantageously enhance wet web strength during processing by allowing fiber-fiber bonding to proceed unimpeded.

### BRIEF DESCRIPTION OF THE FIGURES

[0010] The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in

which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

[0011] FIG. 1 shows a graph comparing strength with starch loading.

[0012] FIG. 2 shows a graph comparing strength with starch retention.

[0013] FIG. 3 shows tensile strength of paper samples.

[0014] FIG. 4 shows results from hydrophobicity tests on paper samples.

[0015] FIG. 5 shows a flow chart for a papermaking system.

[0016] FIG. 6 shows caliper of paper sheets.

[0017] FIG. 7 shows tensile strength and caliper for paper sheets.

### SUMMARY

[0018] Disclosed herein, in embodiments, are systems for papermaking, comprising a population of cellulose fibers dispersed in an aqueous solution and complexed with an activator, and a tether-bearing particulate additive, wherein the addition of the tether-bearing particulate additive attaches the additive to the population of cellulose fibers by the interaction of the activator and the tether. Also disclosed herein in embodiments, is a papermaking precursor comprising a population of cellulose fibers in an aqueous solution wherein the population of cellulose fibers is dispersed in the aqueous solution and wherein the cellulose fibers are complexed with an activator, and wherein the aqueous solution further comprises a tether-bearing particulate additive, wherein the tether-bearing particulate additive attaches to the population of cellulose fibers by an interaction between the activator and the tether. In embodiments, the particulate additive can be an organic additive. In embodiments, the organic additive can comprise starch, and the starch can be a cationic starch or a hydrophobic starch. In other embodiments, the particulate additive can be an inorganic additive.

[0019] Also disclosed herein are systems for papermaking, comprising a first set of processing stations, wherein a papermaking precursor is formed by combining a population of cellulose fibers dispersed in an aqueous solution and complexed with an activator, and a tether-bearing particulate additive, and wherein the addition of the tether-bearing particulate additive attaches the additive to the population of cellulose fibers by the interaction of the activator and the tether; and a second set of processing stations. In embodiments, the particulate additive can be an organic additive. In embodiments, the organic additive can comprise starch, and the starch can be a cationic starch or a hydrophobic starch. In other embodiments, the particulate additive can be an inorganic additive.

[0020] Further disclosed herein are methods for manufacturing a paper product, comprising activating a population of cellulose fibers with an activator, preparing a tether-bearing particulate additive, wherein the tether-bearing particulate additive comprises a tether capable of interacting with the activator; and adding the tether-bearing particulate additive to the activated population of cellulose fibers, thereby attaching the additive to the fibers by the interaction of the activator and the tether. In embodiments, methods are disclosed herein for increasing the strength of a paper product formed from a pulp slurry comprising cellulose fibers, comprising adding an activator polymer to the pulp slurry, forming complexes between the activator polymer and cellulose fibers in the pulp slurry, preparing tether-bearing starch granules, wherein the tether-

bearing starch granules comprise a tether polymer capable of interacting with the activator polymer, and adding the tether-bearing starch granules to the pulp slurry, whereby the starch granules are attached to the cellulose fibers by the interaction of the activator polymer and the tether polymer, thereby increasing the strength of the paper product formed from the pulp slurry. Further disclosed herein are paper products manufactured in accordance with these methods.

[0021] Also disclosed herein, in embodiments, are methods for increasing the bulk of a paper product formed from a pulp slurry comprising cellulose fibers, comprising: providing a first population of cellulose fibers comprising unrefined softwood fibers, forming a first slurry comprising the first population, adding an activator polymer to the first slurry, forming complexes between the activator polymer and the cellulose fibers, providing a second population of cellulose fibers comprising hardwood fibers, forming a second slurry comprising the second population, preparing tether-bearing starch granules, wherein the tether-bearing starch granules comprise a tether polymer capable of interacting with the activator polymer, combining the tether-bearing starch granules with the second slurry whereby the tether-bearing starch granules attach to the hardwood fibers, and adding the second slurry to the first slurry to form a pulp slurry, whereby the starch granules attach the hardwood fibers to the softwood fibers in the pulp slurry, thereby improving a measure of bulk of a paper product formed from the pulp slurry. In certain embodiments, methods are disclosed for increasing the bulk of a paper product formed from a pulp slurry comprising cellulose fibers, comprising providing a cellulose fiber mixture, forming a slurry comprising the cellulose fiber mixture, adding an activator polymer to the slurry to form an activated mixture comprising activated cellulose fibers, preparing tether-bearing starch granules, wherein the tether-bearing starch granules comprise a tether polymer capable of interacting with the activator polymer, combining the tether-bearing starch granules with the activated fiber mixture, whereby the tether-bearing starch granules affix the activated cellulose fibers to each other, thereby increasing the bulk of the paper product formed therefrom. In embodiments, the cellulose fiber mixture comprises hardwood and softwood fibers. In embodiments, the cellulose fiber mixture comprises refined and unrefined fibers. Further disclosed herein are paper products manufactured in accordance with these methods.

### DETAILED DESCRIPTION

[0022] Disclosed herein are systems, precursors, and methods for enhancing the attachment of a particulate additive to a fibrous matrix, so that the particles are efficiently and durably attached to the coarser fibrous matrix. Also disclosed herein are processes for manufacturing a paper product by forming a complex between a particulate additive (such as starch) and the fibers. The invention also encompasses paper made by the processes or method described herein or from a precursor described herein. The systems and methods disclosed herein involve three components: activating the fibers as they are dispersed in a solution, attaching a tethering agent to the particulate additive, and adding the tether-bearing particulate additive to the dispersion containing the activated fibers, so that the additive is attached to the fibers by the interaction of the activating agent and the tethering agent. In embodiments, these systems and methods can be used to treat fibers used in papermaking with a cationic polymer of a specific molecular weight and composition as an activator, to treat starch gran-

ules with an anionic polymer as a tethering agent, and to combine these separately-treated populations so that the starch granules are attached to the pulp fibers.

**[0023]** 1. Activation

**[0024]** As used herein, the term “activation” refers to the interaction of an activating material, such as a polymer, with suspended particles or fibers in a liquid medium, such as an aqueous solution. An “Activator polymer” can carry out this activation. In embodiments, high molecular weight polymers can be introduced into the particulate or fibrous dispersion as Activator polymers, so that these polymers interact, or complex, with the dispersed particles or fibers. The polymer-fiber complexes interact with other similar complexes, or with other fibers, and form agglomerates.

**[0025]** This “activation” step can function as a pretreatment to prepare the surface of the suspended material (e.g., fibers) for further interactions in the subsequent phases of the disclosed system and methods. For example, the activation step can prepare the surface of the suspended materials to interact with other polymers that have been rationally designed to interact therewith in a subsequent “tethering” step, as described below. Not to be bound by theory, it is believed that when the suspended materials (e.g., fibers) are coated by an activating material such as a polymer, these coated materials can adopt some of the surface properties of the polymer or other coating. This altered surface character in itself can be advantageous for retention, attachment and/or dewatering.

**[0026]** In another embodiment, activation can be accomplished by chemical modification of the suspended material. For example, oxidants or bases/alkalis can increase the negative surface energy of fibers or particles, and acids can decrease the negative surface energy or even induce a positive surface energy on suspended material. In another embodiment, electrochemical oxidation or reduction processes can be used to affect the surface charge on the suspended materials. These chemical modifications can produce activated particulates that have a higher affinity for tethered anchor particles as described below.

**[0027]** Suspended materials suitable for modification, or activation, can include organic or inorganic particles, or mixtures thereof. Inorganic particles can include one or more materials such as calcium carbonate, dolomite, calcium sulfate, kaolin, talc, titanium dioxide, sand, diatomaceous earth, aluminum hydroxide, silica, other metal oxides and the like. Organic particles can include one or more materials such as starch, modified starch, polymeric spheres (both solid and hollow), carbon based nanoparticles such as carbon nanotubes and the like. Particle sizes can range from a few nanometers to a few hundred microns. In certain embodiments, macroscopic particles in the millimeter range may be suitable.

**[0028]** In embodiments, suspended materials may comprise materials such as lignocellulosic material, cellulose material, minerals, vitreous material, cementitious material, carbonaceous material, plastics, elastomeric materials, and the like. In embodiments, cellulosic and lignocellulosic materials may include wood materials such as wood flakes, wood fibers, wood waste material, wood powder, lignins, wood pulp, or fibers from woody plants.

**[0029]** The “activation” step may be performed using flocculants or other polymeric substances. Preferably, the polymers or flocculants can be charged, including anionic or cationic polymers.

**[0030]** In embodiments, anionic polymers can be used, including, for example, olefinic polymers, such as polymers made from polyacrylate, polymethacrylate, partially hydrolyzed polyacrylamide, and salts, esters and copolymers thereof (such as sodium acrylate/acrylamide copolymers), sulfonated polymers, such as sulfonated polystyrene, and salts, esters and copolymers thereof. Suitable polycations include: polyvinylamines, polyallylamines, polydiallyldimethylammoniums (e.g., the chloride salt), branched or linear polyethyleneimine, crosslinked amines (including epichlorohydrin/dimethylamine, and epichlorohydrin/alkylenediamines), quaternary ammonium substituted polymers, such as (acrylamide/dimethylaminoethylacrylate methyl chloride quat) copolymers and trimethylammoniummethylene-substituted polystyrene, and the like. Nonionic polymers suitable for hydrogen bonding interactions can include polyethylene oxide, polypropylene oxide, polyhydroxyethylacrylate, polyhydroxyethylmethacrylate, and the like. In embodiments, an activator such as polyethylene oxide can be used as an activator with a cationic tethering material in accordance with the description of tethering materials below. In embodiments, activator polymers with hydrophobic modifications can be used. Flocculants such as those sold under the trademark MAGNAFLOC® by Ciba Specialty Chemicals can be used.

**[0031]** In embodiments, activators such as polymers or copolymers containing carboxylate, sulfonate, phosphonate, or hydroxamate groups can be used. These groups can be incorporated in the polymer as manufactured, alternatively they can be produced by neutralization of the corresponding acid groups, or generated by hydrolysis of a precursor such as an ester, amide, anhydride, or nitrile group. The neutralization or hydrolysis step could be done on site prior to the point of use, or it could occur in situ in the process stream.

**[0032]** The activated suspended material (e.g., fiber) can also be an amine functionalized or modified material. As used herein, the term “modified material” can include any material that has been modified by the attachment of one or more amine functional groups as described herein. The functional group on the surface of the suspended material can be from modification using a multifunctional coupling agent or a polymer. The multifunctional coupling agent can be an amino silane coupling agent as an example. These molecules can bond to a material’s surface and then present their amine group for interaction with the particulate matter. In the case of a polymer, the polymer on the surface of a suspended fiber or particle can be covalently bound to the surface or interact with the surface of the particle and/or fiber using any number of other forces such as electrostatic, hydrophobic, or hydrogen bonding interactions. In the case that the polymer is covalently bound to the surface, a multifunctional coupling agent can be used such as a silane coupling agent. Suitable coupling agents include isocyanate silanes and epoxy silanes as examples. A polyamine can then react with an isocyanate silane or epoxy silane for example. Polyamines include polyallyl amine, polyvinyl amine, chitosan, and polyethyleneimine.

**[0033]** In embodiments, polyamines (polymers containing primary, secondary, tertiary, and/or quaternary amines) can also self-assemble onto the surface of the suspended particles or fibers to functionalize them without the need of a coupling agent. For example, polyamines can self-assemble onto the surface of the particles or fibers through electrostatic interactions. They can also be precipitated onto the surface in the case of chitosan for example. Since chitosan is soluble in acidic aqueous conditions, it can be precipitated onto the

surface of suspended material by adding a chitosan solution to the suspended material at a low pH and then raising the solution pH.

**[0034]** In embodiments, the amines or a majority of amines are charged. Some polyamines, such as quarternary amines are fully charged regardless of the pH. Other amines can be charged or uncharged depending on the environment. The polyamines can be charged after addition onto the suspended particles or fibers by treating them with an acid solution to protonate the amines. In embodiments, the acid solution can be non-aqueous to prevent the polyamine from going back into solution in the case where it is not covalently attached to the particle or fiber.

**[0035]** The polymers or particles can complex via forming one or more ionic bonds, covalent bonds, hydrogen bonding and combinations thereof, for example. Ionic complexing is preferred.

**[0036]** To obtain activated suspended materials, the activator could be introduced into a liquid medium through several different means. For example, a large mixing tank could be used to mix an activating material with fine particulate materials. Activated particles or fibers are produced that can be treated with one or more subsequent steps of attachment to tether-bearing anchor particles.

**[0037]** 2. Tethering

**[0038]** As used herein, the term “tethering” refers to an interaction between an activated suspended particle or fiber and an anchor particle (as described below). The anchor particle can be treated or coated with a tethering material. The tethering material, such as a polymer, forms a complex or coating on the surface of the anchor particles such that the tethered anchor particles have an affinity for the activated suspended material. In embodiments, the selection of tether and activator materials is intended to make the two solids streams complementary so that the activated particles or fibers in the suspension become tethered, linked or otherwise attached to the anchor particle.

**[0039]** In accordance with these systems and methods, the tethering material acts as a complexing agent to affix the activated particles or fibers to an anchor material. In embodiments, a tethering material can be any type of material that interacts strongly with the activating material and that is connectable to an anchor particle.

**[0040]** In embodiments, an anchor particle may comprise materials such as lignocellulosic material, cellulosic material, minerals, vitreous material, cementitious material, carbonaceous material, plastics, elastomeric materials, and the like. In embodiments, cellulosic and lignocellulosic materials may include wood materials such as wood flakes, wood fibers, wood waste material, wood powder, lignins, or fibers from woody plants.

**[0041]** Examples of inorganic particles useful as anchor particles include clays such as attapulgite and bentonite. In embodiments, the inorganic compounds can be vitreous materials, such as ceramic particles, glass, fly ash, PCC, GCC, chalk, TiO<sub>2</sub>, silica, bentonite, kaolin, talc, and the like. The anchor particles may be solid or may be partially or completely hollow. For example, glass or ceramic microspheres may be used as particles. Vitreous materials such as glass or ceramic may also be formed as fibers to be used as particles. Cementitious materials may include gypsum, Portland cement, blast furnace cement, alumina cement, silica cement, and the like. Carbonaceous materials may include

carbon black, graphite, carbon fibers, carbon microparticles, and carbon nanoparticles, for example carbon nanotubes.

**[0042]** In embodiments, plastic materials may be used as anchor particles. Both thermoset and thermoplastic resins may be used to form plastic particles. Plastic particles may be shaped as solid bodies, hollow bodies or fibers, or any other suitable shape. Plastic particles can be formed from a variety of polymers. A polymer useful as a plastic particle may be a homopolymer or a copolymer. Copolymers can include block copolymers, graft copolymers, and interpolymers. In embodiments, suitable plastics may include, for example, addition polymers (e.g., polymers of ethylenically unsaturated monomers), polyesters, polyurethanes, aramid resins, acetal resins, formaldehyde resins, and the like. Addition polymers can include, for example, polyolefins, polystyrene, and vinyl polymers. Polyolefins can include, in embodiments, polymers prepared from C<sub>2</sub>-C<sub>10</sub> olefin monomers, e.g., ethylene, propylene, butylene, dicyclopentadiene, and the like. In embodiments, poly(vinyl chloride) polymers, acrylonitrile polymers, and the like can be used. In embodiments, useful polymers for the formation of particles may be formed by condensation reaction of a polyhydric compound (e.g., an alkylene glycol, a polyether alcohol, or the like) with one or more polycarboxylic acids. Polyethylene terephthalate is an example of a suitable polyester resin. Polyurethane resins can include, e.g., polyether polyurethanes and polyester polyurethanes. Plastics may also be obtained for these uses from waste plastic, such as post-consumer waste including plastic bags, containers, bottles made of high density polyethylene, polyethylene grocery store bags, and the like.

**[0043]** In embodiments, plastic particles for anchor particles can be formed as expandable polymeric pellets. Such pellets may have any geometry useful for the specific application, whether spherical, cylindrical, ovoid, or irregular. Expandable pellets may be pre-expanded before using them. Pre-expansion can take place by heating the pellets to a temperature above their softening point until they deform and foam to produce a loose composition having a specific density and bulk. After pre-expansion, the particles may be molded into a particular shape and size. For example, they may be heated with steam to cause them to fuse together into a lightweight cellular material with a size and shape conforming to the mold cavity. Expanded pellets may be 2-4 times larger than unexpanded pellets. As examples, expandable polymeric pellets may be formed from polystyrenes and polyolefins. Expandable pellets are available in a variety of unexpanded particle sizes. Pellet sizes, measured along the pellet's longest axis, on a weight average basis, can range from about 0.1 to 6 mm.

**[0044]** In embodiments, the expandable pellets may be formed by polymerizing the pellet material in an aqueous suspension in the presence of one or more expanding agents, or by adding the expanding agent to an aqueous suspension of finely subdivided particles of the material. An expanding agent, also called a “blowing agent,” is a gas or liquid that does not dissolve the expandable polymer and which boils below the softening point of the polymer. Blowing agents can include lower alkanes and halogenated lower alkanes, e.g., propane, butane, pentane, cyclopentane, hexane, cyclohexane, dichlorodifluoromethane, and trifluorochloromethane, and the like. Depending on the amount of blowing agent used and the technique for expansion, a range of expansion capabilities exist for any specific unexpanded pellet system. The expansion capability relates to how much a pellet can expand

when heated to its expansion temperature. In embodiments, elastomeric materials can be used as particles. Particles of natural or synthetic rubber can be used, for example.

**[0045]** In embodiments, various interactions such as electrostatic, hydrogen bonding or hydrophobic behavior can be used to affix an activated complex to a tethering material complexed with an anchor particle.

**[0046]** For use in papermaking, an anchor particle can be selected from any particulate matter that is desirably attached to cellulose fibers in the final paper product. The tether-bearing anchor particle comprising the desirable additive can then interact with the activated cellulose fibers in the wet paper stream. As an example, starch granules can be used as an anchor particle to be attached to the cellulose fibers, as is described in more detail below. In other examples, organic and inorganic particulate matter can be attached to cellulose fibers to achieve desired properties. For example, inorganic materials like calcium carbonate, dolomite, calcium sulfate, kaolin, talc, titanium dioxide, sand, diatomaceous earth, aluminum hydroxide, silica, various other metal oxides, and the like, can be used as anchor particles in accordance with these systems and methods. In other embodiments, organic particles such as starch, modified starch, polymeric spheres (both solid and hollow), carbon based nanoparticles such as carbon nanotubes and the like, can be used as anchor particles in accordance with these systems and methods.

**[0047]** In embodiments, polymers such as linear or branched polyethyleneimine can be used as tethering materials. It would be understood that other anionic or cationic polymers could be used as tethering agents, for example polydiallyldimethylammonium chloride (poly(DADMAC)). In other embodiments, cationic tethering agents such as epichlorohydrin dimethylamine (epi/DMA), styrene maleic anhydride imide (SMAI), polyethylene imide (PEI), polyvinylamine, polyallylamine, amine-aldehyde condensates, poly(dimethylaminoethyl acrylate methyl chloride quaternary) polymers and the like can be used. Advantageously, cationic polymers useful as tethering agents can include quaternary ammonium or phosphonium groups. Advantageously, polymers with quaternary ammonium groups such as poly(DADMAC) or epi/DMA can be used as tethering agents. In other embodiments, polyvalent metal salts (e.g., calcium, magnesium, aluminum, iron salts, and the like) can be used as tethering agents. In other embodiments cationic surfactants such as dimethyldialkyl(C8-C22)ammonium halides, alkyl(C8-C22)trimethylammonium halides, alkyl(C8-C22)dimethylbenzylammonium halides, cetyl pyridinium chloride, fatty amines, protonated or quaternized fatty amines, fatty amides and alkyl phosphonium compounds can be used as tethering agents. In embodiments, polymers having hydrophobic modifications can be used as tethering agents.

**[0048]** The efficacy of a tethering material, however, can depend on the activating material. A high affinity between the tethering material and the activating material can lead to a strong and/or rapid interaction there between. A suitable choice for tether material is one that can remain bound to the anchor surface, but can impart surface properties that are beneficial to a strong complex formation with the activator polymer. For example, a polyanionic activator can be matched with a polycationic tether material or a polycationic activator can be matched with a polyanionic tether material. In one embodiment, a poly(sodium acrylate-co-acrylamide) activator is matched with a chitosan tether material.

**[0049]** In hydrogen bonding terms, a hydrogen bond donor should be used in conjunction with a hydrogen bond acceptor. In embodiments, the tether material can be complementary to the chosen activator, and both materials can possess a strong affinity to their respective deposition surfaces while retaining this surface property.

**[0050]** In other embodiments, cationic-anionic interactions can be arranged between activated suspended materials and tether-bearing anchor particles. The activator may be a cationic or an anionic material, as long as it has an affinity for the suspended material to which it attaches. The complementary tethering material can be selected to have affinity for the specific anchor particles being used in the system. In other embodiments, hydrophobic interactions can be employed in the activation-tethering system.

**[0051]** As would be further appreciated by those of ordinary skill, tether-bearing anchor particles could be designed to complex with a specific type of activated particulate matter. The systems and methods disclosed herein could be used for complexing with organic waste particles, for example. Other activation-tethering-anchoring systems may be envisioned for removal of suspended particulate matter in fluid streams, including gaseous streams.

**[0052]** 3. Retention and Incorporation in Papermaking

**[0053]** It is envisioned that the complexes formed from the anchor particles and the activated fibrous matter can form a homogeneous part of a fibrous product like paper. In embodiments, the interactions between the activated suspended fibers and the tether-bearing anchor particles can enhance the mechanical properties of the complex that they form. For example, an activated suspended material can be durably bound to one or more tether-bearing anchor particles, so that the tether-bearing anchor particles do not segregate or move from their position on the fibers. Increased compatibility of the activated fine materials with a denser (anchor) matrix modified with the appropriate tether polymer can lead to further mechanical stability of the resulting composite material.

**[0054]** For papermaking, cationic and anionic polymers for activators and tethering agents (respectively) can be selected from a wide variety of available polymers, as described above. Starch granules or other desirable particles can be selected as anchor particles, where their attachment to pulp fibers would be advantageous. Examples of such desirable particles include, but are not limited to inorganic and organic anchor particles such as have been described above (e.g., for inorganic materials, calcium carbonate, dolomite, calcium sulfate, kaolin, talc, titanium dioxide, sand, diatomaceous earth, aluminum hydroxide, silica, various other metal oxides and the like, and for organic materials, starch, modified starch, polymeric spheres (both solid and hollow), carbon based nanoparticles such as carbon nanotubes and the like). When starch granules are used as anchor particles for attachment to cellulose fibers, they can be used in their native state, or they can be modified with short amine side-groups, with amine polymers, or with hydrophobic side groups (each a "modified starch"). The presence of amines on the surface of the starch granules can help in attaching an anionic tethering polymer.

**[0055]** For activating the cellulose fibers, cationic polymers can be used. The polycation can be linked to the fiber surface using a coupling agent, for example a bifunctional crosslinking agent such as a carbonyldiimidazole or a silane, or the polyamine can self-assemble onto the surface of the cellulose

fiber through electrostatic, hydrogen bonding, or hydrophobic interactions. In embodiments, the polyamine can spontaneously self-assemble onto the fiber surface or it can be precipitated onto the surface. For example, in embodiments, chitosan can be precipitated on the surface of the cellulose fibers to activate them. Because chitosan is soluble only in an acidic solution, it can be added to a cellulose fiber dispersion at an acidic pH, and then can be precipitated onto the surface of the cellulose fibers by slowly adding base to the dispersion until chitosan is no longer soluble. In embodiments, a difunctional crosslinking agent can be used to attach the polycation to the fiber, by reacting with both the polycation and the fiber.

**[0056]** In other embodiments, a polycation such as a polyamine can be added directly to the fiber dispersion or slurry. For example, the addition level of the polycation can be between about 0.01% to 5.0% (based on the weight of the fiber), e.g., between 0.1% to 2%. For example, if the cellulose fiber population is treated with a polyamine like polyDADMAC, a separately treated population of tether-bearing starch granules can be mixed in thereafter, resulting in the attachment of the starch granules to the cellulose fibers by the interaction of the activator polymer and the tether polymer. Starch granules can be treated with a variety of anionic polymers, such as anionic polyacrylamide, which then act as tethers.

**[0057]** While individual retention aids such as polyacrylamide are known in the art to help with the retention of starch granules within a cellulose matrix, the drainage of the paper web is severely affected by the use of these agents individually. The use of a complementary polycation (e.g., polyDADMAC) as an activator, combined with the use of the polyanion as a tether attached to the starch granules in accordance with these systems and methods avoids this problem, reducing the water retention in the paper web and leading to efficient drainage. Furthermore, the use of these systems and methods eliminates the requirement for cooking the starch before using it, thereby eliminating the gelatinizing (“cooking”) step, and decreasing energy utilization.

**[0058]** Starch that is to be treated in accordance with these systems and methods can be further derivatized or coated with moieties that impart desirable properties, e.g., hydrophobicity, oleophobicity or both. Starches thus modified may be also termed “modified starches.” Preferred oil resistant coating formulations are aqueous solutions of cellulose derivatives such as methylcellulose, ethyl cellulose, propyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, ethylhydroxypropyl cellulose, and ethylhydroxyethyl cellulose, cellulose acetate butyrate, which may further comprise polyvinyl alcohol and/or its derivatives. Another group of preferred oil resistant coating compositions are latex emulsions such as the emulsions of polystyrene, styrene-acrylonitrile copolymer, carboxylated styrene-butadiene copolymer, ethylene-vinyl chloride copolymer, styrene-acrylic copolymer, polyvinyl acetate, ethylene-vinyl acetate copolymer, and vinyl acetate-acrylic copolymer. The starch granule thus coated with grease resistant formulations could be attached to the activated pulp fibers via tethering, such that the surface segregation of the starch granule will modify the surface of the paper product.

**[0059]** In embodiments, the presence of hydrophobic starch also improves the hydrophobicity of the resulting paper without needing an internal sizing such as alkyl succinic anhydride (ASA), alkyl ketene dimer (AKD) or Rosin. The gelatinized hydrophobic starch sizes the entire thickness of

the paper. This property is useful in reducing the coating requirements in making coated sheets. The coating applied using a roller or a metering bar or any such methods, would remain on the surface of the paper and not impregnate the bulk of the paper thus needing less coating to achieve the same amount of gloss and surface finish.

**[0060]** In other embodiments, the addition of a coating agent to the starch can improve its mechanical properties such as bending stiffness or tensile strength, or could improve its optical properties (e.g., TiO<sub>2</sub> nanoparticles bound to starch).

**[0061]** 4. Bulk Enhancement

**[0062]** It is known in the art that the use of refined softwood fibers results in a stronger paper matrix than the use of unrefined softwood fibers. The refining process, though, changes the geometry of the long (softwood) fibers from a three-dimensional cylindrical structure to a flat ribbon-like structure. The refining process thus diminishes the overall bulk of the paper product. Refining also requires a significant amount of energy to treat the pulp mechanically to produce the flatter, denser pulp fibers. Paper products are typically formed from a certain percentage of refined pulp, ranging from 0% to 100% refined pulp, to produce a sheet of the desired strength.

**[0063]** It is also known in the art that recycled pulp can be used to form paper products. As used herein, the term “paper products” refers to a product made from natural cellulose fibers, such as hardwood, softwood or recycled fibers. For example, certain paper products for packaging applications can be made from recycled fibers, e.g., cardboard and corrugated board. These packaging products need a combination of bulk and stiffness to be effective during stacked storage and shipment. The recycling process truncates the length of the fibers and reduces both the bulk and strength. One way to improve strength is by refining the recycled fibers which further reduces bulk. Bulking with stiffness improvement also allows for reducing packaging weight by using less fibers to attain a required bulk and stiffness.

**[0064]** Recycled fibers can be derived from hardwood could be made from both hardwood and softwood depending on the source of the paper product.

**[0065]** As used herein, the term “papermaking” refers to the formation of a paper product using hardwood fibers, softwood fibers, recycled fibers or any combination thereof. As used herein, the term “cellulose mixture” refers to any mixture of natural cellulose fibers, whether hardwood, softwood or recycled. A “papermaking precursor” is a solution or mixture comprising cellulose fibers, wherein the solution or mixture has not been subjected to complete drying.

**[0066]** Use of granulated starch, in accordance with the foregoing systems and methods, results in a stronger paper product. In addition, it has been unexpectedly discovered that the use of granulated starch can also reduce or even eliminate the need for refined pulp in papermaking, thereby yielding a higher bulk sheet. A number of processing schemata can be employed to enhance bulk during papermaking in accordance with these systems and methods.

**[0067]** As shown schematically in FIG. 5, an exemplary papermaking system 100 can involve a number of processing stations, 102, 104, 108, 110, 112, 114, 118, 120, and 122. In a pulp mill 102, wood chips are broken down mechanically or chemically, and may be bleached. For recycled paper, the pulp-based components are repulped in a pulp mill 102. Additives may be added to the pulp stream as it exits the pulp mill 102, as shown at Point C. The processed pulp can then proceed to a refiner 104, where the pulp is mechanically treated

to increase surface area of fibers, thereby increasing bonding between fibers, resulting in flatter, denser pulp fibers. Additives may be added to the pulp stream as it exits the refiner **104**, as shown at Point A. The pulp stream can then proceed to a machine chest **108**, where the pulp comes into contact with certain chemicals used in papermaking. This processing station **108** is where multi-stream pulps can meet and become admixed (e.g., hardwood and softwood pulp). Additives may be added to the pulp stream as it exits the machine chest, as shown at Point B. The pulp stream can then proceed to the headbox **110**, where the pulp can be diluted further and released from the headbox onto the forming wire. The first set of processing stations **102-110** comprise the wet end of a papermaking system or machine. The pulp stream can then proceed to a second set of processing stations for forming the paper sheet. These processing stations can include a vacuum section **112**, a press section **114**, a first drying section **118**, a size press **120**, and a second drying section **122**. In the vacuum section **112**, the fiber web can be drained by gravity and then by high vacuum to about 10-15% solids. The fiber web can then proceed to a press section **114**, where the formed fiber web can be pressed through high-pressure rollers to a consistency of about 20-25% solids. The wet paper web can then proceed to a first drying section **118**, where the wet paper web can make contact with steam-heated dryers that contact-dry the sheet up to 98% solids. The paper sheet can then proceed to a size press **120**, where gelatinized starch and other chemicals can be applied to the surface of the paper. The paper sheet can then proceed to a second drying section **122**, where a second set of dryers dry the sheet after it has been wetted in the size press **120**.

**[0068]** In embodiments, additives can be added at Points A, B, and/or C to improve the quality of paper product emerging from a papermaking system **100**. A pulp product combined with the activator polymer and tether-bearing anchor particles as described below is a specific example of a "papermaking precursor." In one embodiment, an activator polymer can be added at Point A, and tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B. In another embodiment, an activator polymer can be added to a softwood stream only at Point A, which can then be admixed with a second stream (e.g., a hardwood stream) in the machine chest **108** or comparable component of the papermaking system **100**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B. In another embodiment, an activator polymer can be added to a hardwood stream only at Point A, which can then be admixed with a second stream (e.g., a softwood stream) in the machine chest **108** or comparable component of the papermaking system **100**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B. In yet another embodiment, an activator polymer can be added to a hardwood stream at Point C, and the activated stream proceeds through the refiner **104**; this activated hardwood stream can be admixed with a second stream (e.g., a softwood stream) in the machine chest **108** or comparable component of the papermaking system **100**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B. In yet another embodiment, an activator polymer can be added to a softwood stream at Point C, and the activated stream proceeds through the refiner **104**; this activated softwood stream can be admixed with a second stream (e.g., a hardwood stream) in the machine chest

**108** or comparable component of the papermaking system **100**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B, or at Point A. In yet another embodiment, an activator polymer can be added to a hardwood stream at Point C, and the activated stream proceeds through the refiner **104**; this activated hardwood stream can be admixed with a second stream (e.g., a softwood stream) in the machine chest **108** or comparable component of the papermaking system **100**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B, or at Point A. In another embodiment, an activator polymer can be added at Point C, and the activated stream proceeds through the refiner **104**. In this embodiment, tether-bearing anchor particles comprising a desirable additive (e.g., a starch) can be added at Point B, or at Point A.

**[0069]** As would be understood by skilled artisans, a combination of hardwood and softwood fibers in a pulp mixture may be desirable, and that a combination of refined and unrefined fibers (either hardwood or softwood) may be desirable. Without being bound by theory, it is understood that unrefined fibers offer bulk and refined fibers offer strength in the final paper sheet. In embodiments, a cellulose fiber mixture containing between about 10% and about 90% hardwood can be used. In other embodiments, a cellulose fiber mixture containing between about 40% and about 80% hardwood can be used. In other embodiments, a cellulose fiber mixture containing between about 60% and about 80% hardwood can be used, or between about 65% and about 75%. In embodiments, a cellulose fiber mixture containing between about 5% and about 75% unrefined fibers can be used. In other embodiments, a cellulose fiber mixture containing between about 20% and about 60% unrefined fibers can be used. In other embodiments, a cellulose fiber mixture containing between about 30% and about 50% unrefined fibers can be used.

#### EQUIVALENTS

**[0070]** While specific embodiments of the subject invention have been discussed, the above specification is illustrative and not restrictive. Many variations of the invention will become apparent to those skilled in the art upon review of this specification. Unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present invention.

#### EXAMPLES

- [0071]** Materials
- [0072]** Market softwood and hardwood pulp
- [0073]** Recycled and deinked pulp from magazine and newsprint
- [0074]** Poly(diallyldimethylammonium chloride), Hi Molecular Weight, 20 wt % in water (polyDADMAC), Sigma-Aldrich, St. Louis, Mo.
- [0075]** MagnaFloc LT30 (PAM) Ciba Specialty Chemicals Corporation, Suffolk, Va.
- [0076]** STA-LOK 356 Starch, Tate & Lyle, Decatur, Ill. (cationic starch granules)

[0077] ChitoClear Chitosan CG800, Primex, Siglufjordur, Iceland

[0078] Lupamin 9095, BASF Corporation, Florham Park, N.J.

[0079] R465 Cationic Starch, Grain Processing Corporation, Muscatine, Iowa

[0080] FilmKote hydrophobic starches, National Starch LLC, Bridgewater N.J.

#### Example 1

##### Control Virgin Pulp

[0081] A 0.5% slurry was prepared by blending 3.5% by weight softwood and hardwood pulp mixture (in the ratio of 20:80) in water.

#### Example 2

##### Control Recycled Pulp

[0082] A 0.5% slurry was prepared by blending 3.1% recycled deinked pulp in water.

#### Example 3

##### Handsheet Preparation

[0083] Handsheets were prepared using a Mark V Dynamic Paper Chemistry Jar and Hand-Sheet Mold from Paper Chemistry Laboratory, Inc. (Larchmont, N.Y.). Handsheets were prepared without addition of polymers as controls, using the control pulps as described in Example 1 and 2. Handsheets were prepared with the addition of polymers as experimental samples, as described below. For preparing each experimental handsheet, the appropriate volume of 0.5% pulp slurry prepared in accordance with Examples 1 or 2 (as applicable) was activated with up to 2% of the selected polymer(s) (based on dry weight), as described below in more detail. Polymer additions were performed at 5 minute intervals. This polymer-containing slurry was diluted with up to 2 L of water and added to the handsheet maker, where it was mixed at a rate of 1100 RPM for 5 seconds, 700 RPM for 5 seconds, and 400 RPM for 5 seconds. The water was then drained off. The subsequent sheet was then transferred off of the wire, pressed and dried.

#### Example 4

##### Tensile Test

[0084] Tensile tests were conducted on control and experimental samples using an Instron 3343. Samples of handsheets for tensile testing were initially cut into 1 in wide strips with a paper cutter, then attached within the Instron 3343. The gauge length region was set at 4 in and the crosshead speed was 1 in/minute. Thickness was measured to provide stress data as was the weight to be able to normalize the data by weight of samples. The strips were tested to failure with an appropriate load cell. At least three strips from each control or experimental handsheet sample were tested and the values were averaged together.

#### Example 5

##### Preparation of Tethered Starches

[0085] Sta Lok 356 or Filmkote starches were dispersed in water such that the solids content was about 20 to 25% to get a slurry of cationic and hydrophobic starches respectively. 1% by weight of anionic polyacrylamide magnafloc LT30 was used as the tethering agent.

#### Example 6

##### Process for Preparing Handsheets from Activated Pulp and Tethered Starch

[0086] 800 ml of a 0.5% pulp slurry prepared in accordance with Example 1 or 2 (as applicable) was initially provided. The pulp slurry was activated with 1% by fiber weight poly-DADMAC. Separately, tethered cationic (or hydrophobic) starch granules were prepared as a slurry in accordance with Example 5. Each slurry was mixed for 5 minutes and then combined and mixed for another 5 minutes using an overhead stirrer. Handsheets were then produced by the method in Example 3. The final paper weight was approximately 4 g for these handsheets.

#### Example 7

##### Starch Retention Measurement

[0087] Starch retention was determined by first analyzing the effluent created after making the handsheets in Example 6. A piece of VWR Grade 413 filter paper with 5  $\mu$ m particle retention was initially dried in an oven at 110 C to remove any moisture and then weighed. The effluent from the handsheet preparation carried out in Example 5 was then filtered through the paper using vacuum filtration. The filter paper was dried again at 110° C. to remove any moisture, and was weighed to determine the lost solids from the handsheet. These solids included the fines from the papermaking process and starch granules. To normalize for only the starch contribution to the effluent, a control experiment was run using the effluent from the preparation of a control pulp using the activator polymer but no starch addition. The filtered solid content in the control effluent was subtracted from the filtered solid content in the starch-bearing effluent, to yield the amount of starch therein. This amount was used to determine the starch retention of the pulp in Example 6.

#### Example 8

##### Effect on Starch Retention of Polymeric Retention Aids Added to Cellulose Pulp-(No Starch Tethering)

[0088] Experiments were carried out to evaluate the starch retention effects of various polymers that can be used to functionalize cellulose fibers. A pulp slurry prepared in accordance with Example 1 was treated with the various polymers listed in Table 1, at the loading levels listed in the Table. The Table lists the effects of the various cellulose fiber polymeric treatments on starch retention, where starch retention was measured in accordance with Example 7. The anionic polyacrylamide (LT 30) resulted in good starch retention, but was observed during the experiment to adversely affected the drainage of water.

TABLE 1

Sample	% Starch Retention
<b>Pulp</b>	
Starch	51%
Chitosan 0.1%	47%
Chitosan 0.5%	37%
Chitosan 1.0%	42%
LT 30 0.1%	75%
LT 30 0.5%	93%
LT 30 1.0%	89%
DADMAC 0.1%	33%
DADMAC 0.5%	31%
DADMAC 1.0%	29%
Polyvinylamine 1.0%	42%

Example 10

#### The Effect of Starch Loading on Strength and Hydrophobicity

**[0090]** Samples were prepared as in Example 6 with tether-bearing Sta Lok 356 starch. Starch retention was measured as set forth in Example 7, and the tensile strength for each sample was measured using an Instron as in Example 4. As set forth in Table 2, certain of the samples were treated with polyDADMAC as activator in concentrations of 1% by solids, and with MagnaFloc LT30 as the tethering agent attached to the starch in concentrations of 1% by solids all in accordance with Example 6. These samples are designated as ATA Process samples in the table below (Table 2).

TABLE 2

#	Fiber Wt (g)	Starch Overall Loading	Starch Amt (g)	ATA Process	Starch in effluent (g)	% Starch Retention	Actual Starch Loading	Tensile Load/Wt
E	4	0%	0.0000	No	0.009		0%	2.62
F	4	17%	0.8007	No	0.318	60%	11%	3.75
G	4	17%	0.8066	Yes	0.014	98%	17%	4.52
H	4	9%	0.4064	No	0.171	58%	6%	3.63
I	4	9%	0.3999	Yes	0.003	99%	9%	4.02
J	4	5%	0.2072	No	0.074	64%	3%	3.46
K	4	5%	0.2019	Yes	0.006	97%	5%	3.56

Example 9

#### The Effect of Starch Loading on Strength

**[0089]** Samples were prepared as in Example 6, where the amount of tether-bearing starch (Sta Lok 356) starch ranged from 0.18 g to 2.0 g, i.e., initial loadings of 4% to 33% of the solids weight. The tether-bearing starch was prepared in accordance with Example 5. Samples were made both with activator and tether and without either activator or tether. For ATA-treated samples, the tether used on the starch was 1% MagnaFloc LT30 by solids and the activator on the pulp was 1% polyDADMAC by solids. Starch retention was measured as set forth in Example 7, and the max load for each sample was measured using an Instron as in Example 4. Data were normalized by the mass to show load contribution per overall solids weight. Graph 1 (FIG. 1) shows the strength improvement with starch loading with and without the ATA process chemistry. For all samples functionalized with the ATA chemistry described in Example 6, the starch granule retention was >98%. Without being bound by theory, it is understood that the inclusion of untethered starch in the unactivated paper matrix is limited by the amount of physical entanglements between starch and cellulose, reflected in the plateau in strength measurement with higher loads of starch added without ATA processing. With ATA, a greater amount of starch can be attached effectively to the cellulose, progressively increasing strength as shown in FIG. 1. As the amount of ATA-bound starch increases, it yields a maximum benefit in strength, which then decreases at higher loadings. It is hypothesized that the higher loadings beyond the maximum exceed the capacity of the hydrogen bonding network of the cellulose fibers.

**[0091]** Graph 2 (FIG. 2) illustrates the effect of starch retention on the strength of the paper. Graph 2 compares the difference between strength of the handsheets made with the ATA Process compared to handsheets that have not been treated with any polymer addition.

Example 11

#### Effect of Hydrophobic Starch Loading on Strength of Paper Made with Recycled Fibers

**[0092]** Recycled fibers are relatively weak due to fiber length reduction during fiber recovery and processing. In this example, the ATA process is applied to improve the strength of handsheets made from recycled fibers by incorporating starch within the fibrous web. To produce handsheets of recycled paper using the ATA process, a recycled pulp slurry prepared in accordance with Example 3 was treated in accordance with Example 6, using Filmkote hydrophobic starches as tether-bearing starches. Filmkote starches of varying degrees of hydrophobicity were used, as set forth in Graph 3 (FIG. 3). For example, the starch Filmkote 550 is more hydrophobic than Filmkote 54. The tensile strength of the paper samples was measured as set forth in Example 4. As shown in Graph 3 (FIG. 3), the ATA process as applied to recycled paper improved the strength of the paper samples by amounts from about 25-40%.

Example 12

#### Effect of Hydrophobic Starch Loading on Hydrophobicity of Paper Made with Recycled Fibers

**[0093]** Using recycled fiber handsheet samples prepared as in Example 11, hydrophobicity was tested by depositing a 15

microliter water droplet on the surface of the paper and recording the time for the droplet to completely absorbed by the paper. The results of the hydrophobicity tests are shown in Graph 4 (FIG. 4). These results demonstrate that the use of the ATA process to attach hydrophobic starches to recycled pulp fibers improves the water resistance of the paper by nearly 500% compared to control samples having no added no starch.

#### Example 13

##### Control Unrefined Virgin Pulp

**[0094]** A 0.3% slurry was prepared by blending 14% by weight unrefined softwood and hardwood pulp mixture (in the ratio of 30:70) in water.

#### Example 14

##### Control Refined Virgin Pulp

**[0095]** A 0.3% slurry was prepared by blending 3.5% by weight refined softwood and hardwood pulp mixture (in the ratio of 30:70) in water.

#### Example 15

**[0096]** Handsheets were prepared using a Mark V Dynamic Paper Chemistry Jar and Hand-Sheet Mold from Paper Chemistry Laboratory, Inc. (Larchmont, N.Y.). Handsheets were prepared without addition of polymers as controls, using the control pulps as described in Examples 14 and 15 and mixtures of the two. Handsheets were prepared with the addition of polymers as experimental samples, as described below. For preparing each experimental handsheet, the appropriate volume of 0.3% pulp slurry prepared in accordance with Examples 13 or 14 or mixtures of the two (as applicable) was activated with up to 2% of the selected polymer(s) (based on dry weight), as described below in more detail. Polymer additions were performed at 5 minute intervals. This polymer-containing slurry was diluted with up to 2 L of water and added to the handsheet maker, where it was mixed at a rate of 1100 RPM for 5 seconds, 700 RPM for 5 seconds, and 400 RPM for 5 seconds. The water was then drained off. The subsequent sheet was then transferred off of the wire, pressed and dried.

#### Example 16

##### Preparation of Tethered Starch

**[0097]** Penford Douglas Pearl starch were dispersed in water such that the solids content was about 20 to 25%. 1% by weight of anionic polyacrylamide Magnafloc 919 was used as the tethering agent.

#### Example 17

##### Process for Preparing Handsheets from Activated Pulp and Tethered Starch

**[0098]** 1000 ml of a 0.3% pulp slurry prepared in accordance with Example 13 or 14 or a mixture of the two (as applicable) was initially provided. The pulp slurry was activated with 0.1% by fiber weight polyDADMAC. Separately, starch granules were prepared as a slurry III in accordance with Example 16. Each slurry was mixed for 5 minutes and then combined and mixed for another 5 minutes using an

overhead stirrer. Handsheets were then produced by the method in Example 15. The final paper weight was approximately 3 g for these handsheets.

#### Example 18

##### Caliper Analysis of Refined and Unrefined Pulp Handsheets

**[0099]** Handsheets prepared in Example 17 were each cut into strips and stacked to measure the caliper of 10× that of a single handsheet. The calipers were normalized by basis weight and compared to one another in Table 3 below. These results are also shown in FIG. 6.

TABLE 3

Caliper Analysis				
Condition	Average 10x caliper in.	Sheet weight g	Caliper/Weight in./g	Normalized to control inch/g * g/inch
Control refined (no starch)	0.170	4.14	0.0410	1.00
Control unrefined (no starch)	0.141	2.63	0.0534	1.30
Unrefined + 8% Starch with ATA	0.151	2.76	0.0548	1.34

#### Example 19

##### Tensile Strength and Bulk Enhancement with Starch Granule Attachment

**[0100]** The data illustrated in FIG. 7 show the results of tensile strength measurements and bulk measurements conducted on handsheet samples prepared with a mixture of 70% unrefined and 30% refined fiber mixture with and without starch granule addition of 8% by weight of the fibers and with and without the use of anchor-tether chemistry. The results demonstrate that the ATA chemistry enhances the strength of the handsheets made with a mixture of refined and unrefined fibers compared to 100% unrefined fiber sheet and the one made without ATA chemistry. The strength is comparable to the sheet made with 100% refined fibers while showing an effective bulk increase of ~10%.

**[0101]** While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

1. A method of increasing the bulk of a paper product formed from a pulp slurry comprising cellulose fibers, comprising:

- providing a first population of cellulose fibers comprising unrefined softwood fibers,
- forming a first slurry comprising the first population,
- adding an activator polymer to the first slurry, forming complexes between the activator polymer and the cellulose fibers,
- providing a second population of cellulose fibers comprising hardwood fibers,
- forming a second slurry comprising the second population,

- preparing tether-bearing starch granules, wherein the tether-bearing starch granules comprise a tether polymer capable of interacting with the activator polymer, combining the tether-bearing starch granules with the second slurry whereby the tether-bearing starch granules attach to the hardwood fibers, and adding the second slurry to the first slurry to form a pulp slurry, whereby the tether-bearing starch granules attach the hardwood fibers to the softwood fibers in the pulp slurry, thereby improving a measure of bulk of a paper product formed from the pulp slurry.
2. The method of claim 1, wherein the bulk is increased without a loss of strength.
  3. A method of increasing the bulk of a paper product formed from a pulp slurry comprising cellulose fibers, comprising:
    - providing a cellulose fiber mixture,
    - forming a slurry comprising the cellulose fiber mixture,
    - adding an activator polymer to the slurry to form an activated mixture comprising activated cellulose fibers,
    - preparing tether-bearing starch granules, wherein the tether-bearing starch granules comprise a tether polymer capable of interacting with the activator polymer,
    - combining the tether-bearing starch granules with the activated fiber mixture, whereby the tether-bearing starch granules affix the activated cellulose fibers to each other, thereby increasing the bulk of the paper product formed therefrom.
  4. The method of claim 3, wherein the cellulose fiber mixture comprises recycled fibers.
  5. The method of claim 3, wherein the cellulose fiber mixture comprises hardwood and softwood fibers.
  6. The method of claim 4, wherein the cellulose fiber mixture comprises refined and unrefined fibers.
  7. The method of claim 5, wherein the cellulose fiber mixture comprises about 40% to about 80% of hardwood fibers.
  8. The method of claim 5, wherein the cellulose fiber mixture comprises from about 60% to about 80% hardwood fibers.
  9. The method of claim 5, wherein the cellulose fiber mixture comprises from about 65% to about 75% hardwood fibers.
  10. A paper product formed according to the method of claim 1.
  11. A papermaking precursor comprising a population of cellulose fibers in an aqueous solution wherein:
    - the population of cellulose fibers is dispersed in the aqueous solution and
    - wherein the cellulose fibers are complexed with an activator, and
    - wherein the aqueous solution further comprises a tether-bearing particulate additive,
    - wherein the tether-bearing particulate additive attaches to the population of cellulose fibers by an interaction between the activator and the tether.
  12. The precursor of claim 11, wherein the additive is an organic additive.
  13. The precursor of claim 12, wherein the organic additive comprises a starch.
  14. The precursor of claim 13, wherein the starch comprises a cationic starch.
  15. The precursor of claim 13, wherein the starch comprises a hydrophobic starch.
  16. The precursor of claim 11, wherein the additive is an inorganic additive.
  17. A paper product formed by subjecting the papermaking precursor of claim 11 to a papermaking process comprising drying.
  18. A system for papermaking, comprising:
    - a first set of processing stations, wherein a papermaking precursor is formed by combining a population of cellulose fibers dispersed in an aqueous solution and complexed with an activator, and a tether-bearing particulate additive, and wherein the addition of the tether-bearing particulate additive attaches the additive to the population of cellulose fibers by the interaction of the activator and the tether; and
    - a second set of processing stations.
  19. The system of claim 18, wherein the additive is an organic additive.
  20. The system of claim 19, wherein the organic additive comprises a starch.
  21. The system of claim 20, wherein the starch comprises a cationic starch.
  22. The system of claim 20, wherein the starch comprises a hydrophobic starch.
  23. The system of claim 18, wherein the additive is an inorganic additive.

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