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(54) **PROCESS FOR MAKING ABRASION
RESISTANT PAPER AND PAPER AND PAPER
PRODUCTS MADE BY THE PROCESS**

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(57) **ABSTRACT**

In this papermaking process, a first strength agent is added to a stock suspension containing pulp and optionally other additives prior to its being formed into a web at the wet end of a papermaking machine. The web is then formed and processed into paper. A second strength agent is then applied to the surface of the paper. The strength agents may be selected to have opposite charge.

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**PROCESS FOR MAKING ABRASION RESISTANT
PAPER AND PAPER AND PAPER PRODUCTS
MADE BY THE PROCESS**

**CROSS-REFERENCE TO RELATED
APPLICATION**

[0001] This application claims the benefit of provisional application Ser. No. 60/514279, filed Oct. 24, 2003 which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to papermaking and, more particularly, to processes for making paper having improved properties such as abrasion resistance, decreased coefficient of friction, and increased brightness.

BACKGROUND OF THE INVENTION

[0003] The surface strength of manufactured paper products is receiving increased attention as papermaking technology advances and the paper products produced thereby find an ever-growing field of use. Poor surface strength has numerous repercussions on papermaking machinery and on the products themselves. Paper products having a low surface strength can bind or catch on rollers during the manufacturing process causing costly delays and waste of materials. Similarly, paper that is used as a component of a commercial product, such as the backing paper for gypsum wallboard, ideally should have a high surface strength in order to prevent tearing or damage to the core components as well as to prevent catching or binding on conveyor belts during the various steps of product manufacture and transportation. Consequently, it would be highly desirable to be able to manufacture paper having an increased surface strength in order to improve abrasion resistance, especially when the paper is to be used as backing paper in abuse resistant wallboard products.

[0004] A variety of different solutions have been proposed to solve or minimize the problem of abrasion resistance on the surfaces of paper. For example, U.S. Pat. No. 6,083,586 describes compositions and methods for the manufacture of material sheets having a starch-bound matrix, optionally reinforced with fibers and inorganic mineral filler.

[0005] U.S. Pat. No. 6,153,040 discloses a process for reducing the rollups in gypsum board panels when the panels are laminated. At least one face of the gypsum board paper is treated with a friction reducing agent, such as a wax or wax emulsion, in order to reduce its coefficient of friction, resulting in the reduction of shear force which develops between the backing paper of a gypsum board panel and the conveyor belts used to carry such a panel.

[0006] The addition of cationic wet-strength polyamide resins to paper cover sheets, especially polyamide epichlorohydrin resin, is described in U.S. Pat. No. 6,489,040.

[0007] U.S. Pat. No. 6,517,674 describes a process for manufacturing wear resistant/abrasion resistant paper incorporating spacer- or separator-particles to minimize the amount of surface damage on the paper surface. The particles described and incorporated into the paper are microspheres, such as glass microspheres, and abrasion resistant particles of grit such as aluminum oxide or silicon carbide. According to the '674 patent, the particles are added to the

paper fiber pulp at the wet end of the paper machine from a primary or secondary headbox using a curtain slot coater as the application device.

[0008] In the process taught in U.S. Pat. No. 6,551,457, paper is produced from an aqueous suspension containing cellulosic fibers and optional fillers. After draining the suspension, the obtained paper web is passed through the nip of a paper manufacturing machine. A chemical system comprising a polymeric component and a micro- or nanoparticle component is added to the paper suspension/web. The addition of such a mixture of components is said to improve the overall quality and strength of the paper product, such as its coefficient of friction.

[0009] U.S. Pat. No. 6,562,444 discloses a fiber-cement and gypsum laminate composite building material that contains an adhesive layer interposed between the fiber-cement sheet and the gypsum panel, so as to improve the abrasion resistance of the laminate. The adhesive layer is a polymeric adhesive, such as modified starches.

[0010] U.S. Pat. No. 6,568,148 discloses a covering element for building surfaces and a method for the production of such an element. The covering element is described as having an upper face with a support layer made up of cellulose in which an abrasion-resistant material, such as corundum particles, is embedded, thereby providing enhanced abrasion resistance and a lowered coefficient of friction.

[0011] The literature has also reported several approaches to the problem of abrasion resistance in papers. Zhang, et al. in *Wear*, Vol. 253 (2002), pp. 1086-1093 ("Effect of Particle Surface Treatment on the Tribological Performance of Epoxy Based Nanocomposites") describes the preparation of modified nanosilica covalently bonded to polyacrylamide particles, thereby increasing the interfacial interaction between particles and matrix, and resulting in reductions in surface abrasion. Gumagul, et al. described factors affecting the coefficient of friction of paper, and suggested that the coefficient of friction is a function of the amount of extractives present in or on a paper surface (*Journal of Applied Polymer Science*, Vol. 46 (1992), pp. 805-814; "Factors Affecting the Coefficient of Friction of Paper"). According to the article, the amount and identity of the particles significantly effect the coefficient of friction. Finally, a review describing the effect of fillers on the coefficient of friction in papers was detailed in *TAPPI Journal*, Vol. 74 (1991), pp.341-347 ("Effect of Fillers on Paper Friction Properties"), describing how the use of various fillers such as kaolin, talc, and synthetic precipitated silica in the paper manufacturing process can effect the coefficient of friction.

[0012] While it is known that the addition of small, hard abrasion resistant particles (also referred to as "grit") to the paper, or to resin mixtures which coat the sheet, can enhance the abrasion resistance of papers, paper products and high-pressure laminates, their use is often accompanied by costly side effects. For example, the use of alumina has been reported to give wear resistance of 400 to 600 cycles. However, the use of abrasion resistant particles, even micro-particles or nanoparticles, tend to scratch and cause significant damage to highly polished caul plates and rollers used during the paper production process for producing both high pressure and low pressure products. Rollers and caul plates scratched or otherwise damaged through contact with abra-

sion resistant materials such as described above must either be resurfaced or replaced at a significant cost

[0013] In view of the foregoing, it will be appreciated that there is a need for abrasion resistant paper, and a process for producing such abrasion resistant paper that avoids damage to the papermaking machinery caused by incorporation of grit into the paper.

SUMMARY OF THE INVENTION

[0014] The present invention provides a process for making paper as well as paper and paper products made by the process. In this papermaking process, a first strength agent is added to the stock suspension containing pulp and optionally other additives prior to its being formed into a web at the wet end of a papermaking machine. The web is then formed and processed into paper. A second strength agent is then applied to the surface of the paper. In this process, the strength agents are selected to have opposite charge (or to be amphoteric). Thus, in one embodiment, for example, the first strength agent is a cationic dry-strength agent and the second strength agent is an anionic dry-strength agent.

[0015] The process of this invention can be used to make paper that is resistant to abrasion. Embodiments of this process produce paper having other desirable physical properties like high optical brightness and a low friction surface. An optically bright paper can be obtained by applying the second strength agent in a solution that also contains an optical brightener. A paper having a low friction surface can be obtained by including a hydrophobic organo-silicone in the solution that is used to apply the second strength agent.

[0016] Paper made by the process is useful in a variety of paper products. In particular, the process is useful for making abrasion resistant backing paper for gypsum wall-board.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] Where not expressly defined, the terms used in this disclosure are intended to be construed as those skilled in the art would understand them. The following express definitions are consonant with the understanding of those skilled in the art.

[0018] "Paper", as used herein, refers to a web of pulp fibers that are formed from an aqueous suspension on a wire or screen and held together at least in part by hydrogen bonding, and which can be made by hand or by machine. Included in this definition are the wide range of matted or felted webs of vegetable fiber (mostly wood) that have been formed on a screen from a water suspension, such as "tree paper" manufactured from wood pulp derived from trees, "plant papers" or "vegetable papers" which include a wide variety of plant fibers (also known as "secondary fibers"), such as straw, flax, and rice fibers, and is broadly referred to as "cellulose-based paper", and Kraft paper (paper manufactured by the Kraft process). Further, the term paper as used herein is meant to refer to products containing substantially all virgin pulp fibers, substantially all recycled pulp fibers, or both virgin and recycled pulp fibers.

[0019] "Papermaking machine", as used herein, refers to any of the papermaking machines known in the art, all of which are suitable for use with the process of the present

invention. Such machines include cylinder machines, four-drinier machines, twin wire forming machines, FC Former machines, and modifications thereof.

[0020] "Pulp" refers to fibers that are plant based, including but not limited to wood and similar "woody" plants, soy, rice, cotton, straw, flax, abaca, hemp, bagasse, lignin-containing plants, and the like. Such pulps include, but are not limited to, thermomechanical pulps, bleached thermomechanical pulps, chemi-thermomechanical pulps (CTMP), bleached chemi-thermomechanical pulps, and deinked bleached thermomechanical pulps.

[0021] "Sheet", as used herein, is intended to include any substantially flat, corrugated, curved, bent, or textured sheet made using the compositions and methods described herein. The sheets can have greatly varying thickness depending on the particular application for which the sheet is intended. That is, the sheets can be as thin as about 0.01 mm and as thick as 1 cm or greater, where strength, durability, and/or bulk are important considerations depending upon the end use of the paper sheet.

[0022] "Stock suspension", as used herein, refers to a mixture, or slurry, of pulp, fillers, water, and other papermaking materials. As used herein, the term "stock suspension" is meant to be equivalent to the term "pulp slurry".

[0023] "Strength agent" refers to compounds that are incorporated into paper in order to increase its resistance to tearing. "Wet-strength agents" are agents that make paper more resistant to tearing when the paper is wet. "Dry-strength agents" are agents that make the paper more resistant to tearing when the paper is dry, but are less effective at strengthening wet paper than wet-strength agents are. Dry-strength agents can be cationic, anionic or amphoteric in nature.

[0024] "Web", as used herein, refers to the continuous mat of fibers that is deposited on the wire or felt, drained, pressed and dried to form paper.

[0025] The present invention provides a process for making paper. The paper and paper products made by the process may exhibit improved surface strength, abrasion resistant, a low friction surface and/or a high optical brightness depending upon the particular embodiment of the process that is followed.

[0026] The process of the present invention can be practiced on conventional papermaking equipment. Although papermaking equipment varies in operation and mechanical design, the processes by which paper is made on different equipment contain common stages. Papermaking includes a pulping stage, stock preparation stage, a wet end stage and a dry end stage.

[0027] In pulping, individual cellulose fibers are liberated from a source of cellulose such as wood either by mechanical or chemical action, or both.

[0028] The liberated fibers, or pulp, is suspended in water in the stock preparation stage. Additives such as brightening agents, dyes, pigments, fillers, antimicrobial agents, defoamers, pH control agents and drainage aids also may be added to the stock at this stage. As the term is used in this disclosure "stock preparation" includes such operations as dilution, screening and cleaning of the stock suspension that

may occur prior to forming of the web. In particular, it includes feeding the pulp stream to a fan pump from a machine chest.

[0029] The wet end stage commences after preparation of the stock suspension. For purposes of this disclosure, the wet end stage commences when the pulp first contacts a wire or felt in a papermaking machine. The wet end stage further includes such later operations as forming of the web, draining of the web and consolidation of the web (pressing).

[0030] In the dry end stage, the web is dried and may be subjected to additional processing like size pressing, calendering, spray coating of surface modifiers, printing, cutting, corrugating and the like.

[0031] Of relevance to the present invention, a size press is a device for applying a solution to the paper. It includes a pair of squeeze rolls which are moistened with the solution sought to be applied. The size press typically is situated between drying sections to allow removal of excess moisture. Size presses are typically used to apply surface sizing to improve the water resistance of the paper and improve ink absorption.

[0032] A calender stack is a series of solid rolls, usually made of steel or iron through which the dry paper is passed in a serpentine manner. Pressure applied to the paper as it passes between rolls in the calender stack can improve surface smoothness, increase gloss, make the caliper of the paper more uniform and decrease porosity. Of relevance to the present invention, a nip (or multiple nips) between calender rolls may be flooded in a "waterbox" application. The calender waterbox may be used to apply coatings to the paper for a variety of purposes, such as to increase water resistance, reduce curl and improve gloss.

[0033] In addition to a size press and calender waterbox, the dried paper can be coated by spray coating using a sprayboom.

[0034] Three general types of papermaking machines that are routinely used in the papermaking industry are differentiated by the way that they form the web. In a fourdrinier papermaking machine, the web is formed by delivering a ribbon of stock suspension to a porous belt known to those skilled in the art as the "wire" from a headbox. The headbox is a tank positioned above or beside the wire. The wire is drawn between a "breast roll" and a "couch roll" and is typically driven by the couch roll. The headbox is typically positioned above the wire near the breastroll. The web is delivered from the headbox to the wire through a narrow opening in the headbox that is known to those skilled in the art as the "slice." As the wire travels, the web is drawn towards the couch roll. While in transit, water drains from the pulp through the porous wire under the effect of gravity and typically with the assistance of tube rolls, hydrofoils and/or suction boxes. From the wire, the web is passed to the pressing section of the paper machine. The web typically has a consistency of from about 12% to about 25% before pressing. In the pressing section, the web is squeezed between press rolls to eliminate more water. From the pressing section, the partially dried web is passed to the drying section. There, the web is dried, typically to a moisture content of from about 4% to about 12% by passing over heated dryer cans, although many papermachines in the gypsum industry dry to 0% to about 1% moisture content for greater dimensional stability.

[0035] Another common papermaking machine is the cylinder machine. The stock suspension is fed into one or more vats. In each vat, there is a horizontally disposed cylinder having a wire around its circumference. The cylinder is partially immersed in the stock suspension. The cylinder is rotated. As it does so, the wire picks up fibers, carries them out of the stock suspension and delivers them to a "pick-up felt." The pick-up felt is a porous belt that travels synchronously with the cylinder. In a multiple cylinder machine, multi-ply paper can be made by supplying a different stock suspension to each vat. The web is then transferred from the pickup felt to the pressing section and then to the drying section.

[0036] In another common design, the stock suspension is sprayed between two converging wires. Such twin wire formers accelerate the removal of water making them well suited for high speed machines.

[0037] It has been found that adding a cationic dry-strength agent prior to the wet stage of the papermaking process and an anionic dry-strength agent during the dry stage of the papermaking process yields paper having an increased surface strength.

[0038] Accordingly, the present invention provides a process for making paper and paper products comprising the steps of (1) preparing a stock suspension of cellulosic fibers, (2) adding a first strength agent to the stock suspension, (3) forming the cellulosic fibers into a substantially uniform web and (4) drying the web into paper and applying a second strength agent to the surface of the paper. The first strength agent is either a cationic dry-strength agent, an amphoteric dry-strength agent, or a cationic wet-strength agent, with cationic dry-strength agents being preferred. The second strength agent is either an anionic dry-strength agent or an amphoteric dry-strength agent, with anionic dry-strength agents being preferred.

[0039] Cationic dry-strength agents useful in practice of the present invention include, but are not limited to, cationic polyacrylamides, natural polymers, modified natural polymers, synthetic polymers, starches modified to have quaternary ammonium functional groups, celluloses, natural gums, polyvinyl alcohol, and any number of commercially available compounds having dipolar functional groups that allow for the formation of hydrogen bonds. Preferred cationic dry-strength agents are cationic polyacrylamides and cationic synthetic polymers. As those skilled in the art appreciate, a cationic polyacrylamide can be made by co-polymerization of acrylamide with another acrylic monomer having a quaternary ammonium substituent thereon, such as $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CHCH}_2$. An example of a commercially available cationic polyacrylamide is Nalco 997, available from Nalco Chemical Company (Naperville, Ill.).

[0040] Anionic dry-strength agents useful in practice of the present invention include, but are not limited to, anionic polyacrylamides, natural starches, and carboxymethylcellulose (CMC). The most preferred anionic dry-strength agents are anionic polyacrylamides. As those skilled in the art appreciate, an anionic polyacrylamide can be made by co-polymerization of acrylamide with an anionic acrylic monomer such as sodium acrylate. An example of a commercially available anionic polyacrylamide is Nalco 1044, available from Nalco Chemical Company (Naperville, Ill.).

[0041] In an alternative embodiment, either the cationic dry-strength agent or the anionic dry-strength agent, or both,

is substituted by an amphoteric dry-strength agent, such as amphoteric starches. Amphoteric compounds useful in practice of the present invention have a ratio of anionic groups to cationic groups of from about 0.1:1.0 to about 1.0:1.0. Preferably, the amphoteric compounds have a ratio of anionic groups to cationic groups of about 1.0:1.0. For example, ratios of anionic groups to cationic groups in amphoteric compounds suitable for use with the present disclosure include ratios of about 0.1:1.0, about 0.2:1.0, about 0.3:1.0, about 0.4:1.0, about 0.5:1.0, about 0.5:1.0, about 0.6:1.0, about 0.7:1.0, about 0.8:1.0, about 0.9:1.0, about 1.0:1.0, and ratios that fall between any two of these ratios.

[0042] In yet another alternative embodiment, the cationic dry-strength agent is substituted by a cationic wet-strength agent. Wet-strength agents are typically thermosetting resins that are added to the stock suspension, web or paper in order to impart wet-strength to the paper product. They also often contribute to the dry-strength of the paper. Wet-strength agents are often cationic thermosetting resins, and are typically added to the stock prior to being sent to the paper machine. By thermosetting, it is meant that upon drying and/or heating, the wet-strength resins form a substantially insoluble, and water-resistant, network which can withstand wetting of the paper, thus contributing to the wet-strength of the paper. Generally speaking, wet-strength agents are polymeric, polar enough to be soluble or substantially dispersible in water, cationic so as to be substantive to pulp, and reactive/thermosetting. The types of wet-strength agents useful in the practice of the present invention include acid-curing resins, neutral to acid curing resins, and neutral to alkaline curing resins. Useful acid-curing, or formaldehyde-based, resins include urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins, and other resins which can be used at a system pH between about pH 4 and pH 5. Neutral to acid curing resins that are useful as wet-strength agents in the practice of the present invention include dialdehyde starch (DAS), polyacrylamide-glyoxal (PAMG) resins, and aldehyde-modified starches. Neutral/alkaline curing resins that are useful as wet-strength agents polyamide-epichlorohydrin resin (PAE), resins containing at least one epoxide functional group, and derivatives of the reaction of epichlorohydrin with a polyamine resin.

[0043] The cationic, anionic and amphoteric dry-strength agents, as well as the wet-strength agents, preferably have a specific gravity of from about 1.00 to about 1.20, and more preferably a specific gravity of from about 1.01 to about 1.10. Most preferably, the specific gravity is from about 1.02 to about 1.08. The dry-strength agents preferably have a viscosity of from about 1,000 cps (1 Pa-s) to about 15,000 cps (15 Pa-s), and more preferably of from about 2,000 cps (2 Pa-s) to about 14,000 cps (14 Pa-s).

[0044] The cationic dry-strength agents added prior to the wet end (e.g., fed to the liner thick stock) can be added in an amount of from about 1 lbs/ton (of total paper) (0.5 kg/t) to about 40 lbs/t (9.1 kg/t), and more preferably from about 5 lbs/ton (2.3 kg/t) to about 15 lbs/t (6.8 kg/t). For example, the cationic dry-strength agents added prior to the wet end of the manufacturing process can be added in an amount of about 1 lb/t (0.5 kg/t), about 2 lb/t (0.9 kg/t), about 3 lb/t (1.4 kg/t), about 4 lb/t (1.8 kg/t), about 5 lb/t (2.3 kg/t), about 6 lb/t (2.7 kg/t), about 7 lb/t (3.2 kg/t), about 8 lb/t (3.6 kg/t), about 9 lb/t (4.1 kg/t), about 10 lb/t (4.5 kg/t), about 15 lb/t

(6.8 kg/t) and about 20 lb/t (9.1 kg/t), as well as in ranges between any two of these values. When the cationic dry-strength agent is Nalco 997, it is preferably added at a rate of about 10 lbs/ton dry.

[0045] The anionic dry-strength agents are added at the dry end (e.g., in the calender waterbox) in an amount of from about 5 lbs/ton (of liner plies) (2.3 kg/t) to about 25 lbs/ton (11.3 kg/t), and more preferably from about 6 lbs/t (2.7 kg/t) to about 20 lbs/ton (9.1 kg/t). The dry-strength agents added at the dry end of the manufacturing process can be added in an amount of from about 5 lb/t (2.3 kg/t), about 6 lb/t (2.7 kg/t), about 7 lb/t (3.2 kg/t), about 8 lb/t (3.6 kg/t), about 9 lb/t (4.1 kg/t), about 10 lb/t (4.5 kg/t), about 15 lb/t (6.8 kg/t), about 20 lb/t (9.1 kg/t), and about 25 lb/t (11.3 kg/t), as well as in ranges between any two of these values. When the anionic dry-strength agent is Nalco 1044, it is preferably added at a rate of about 2 lbs/ton dry.

[0046] The dry-strength agents can be added in one portion, or in increments over a predetermined period of time. For example, the cationic dry-strength agent can be added prior to the wet end of the papermaking machine in substantially one portion, or charge. Preferably, the cationic dry-strength agent is added to the wet end incrementally in predetermined amounts over a period of time.

[0047] A typical process for the manufacture of a paper product having increased surface strength in accordance with the present invention is as follows. A suspension of pulp and fibers is prepared and additives, as necessary, are added in. A cationic dry-strength agent or agents can be added at this point. The pulp is 'formed', or applied to the wire at a consistency suitable to give good formation. That is, the stock is applied such that an even distribution of fibers results, allowing for the generation of a paper product of uniform thickness. This is accomplished by circulating the stock suspension into a headbox so that the stock is delivered as a substantially uniform web of pulp onto the wire through the slice at a velocity substantially equivalent to that of the wire. An optional secondary headbox can be provided to deliver a top coat of higher-quality fiber onto the primary paper product sheet as it moves down the production line.

[0048] Following deposition of the stock suspension from the headbox onto the moving wire, the web is carried over rolls (such as breast rolls, table rolls, and couch rolls) and suction boxes, and off the table. As the paper web is transported on the wire, the sheet loses water by drainage and through the suction boxes, and optionally through foils, lovals, vacuum units, and the like.

[0049] Water is further removed from the web by pressing and drying. Drying can be accomplished through the use of drying devices such as dryer cans (hollow, revolving, steam-filled drums), dryer felts, steam control systems, pocket ventilation systems, dryer hoods, Yankee dryers drums, impulse drying, combinations thereof, and the like. The choice of type of drying means will generally depend upon the machine and/or the type of paper product being manufactured. Sizing, defoamers, and the like can be added using one or more size presses located between dryer sections.

[0050] The paper then passes through a waterbox-equipped calender stack, where an anionic dry-strength agent or agents are added. Optionally, a hydrophobic organo-silicone compound in combination with the anionic

dry-strength agent and an optical brightener are fed into the waterbox, and are consequently applied to the paper as it passes through the calender stack waterbox.

[0051] As further illustrated in Example 1, which follows, paper and paper products made by the process of this invention exhibit improved surface strength. Normal gypsum facing paper will lose ~0.009" in 100 to 200 cycles of abrasion while paper made according to our process loses only 0.000 to 0.005" after 1000 cycles. Surface strength was measured using a modification of the procedure specified in ASTM D 4977-98b.

[0052] One particular embodiment of the inventive process yields a paper with a surface having a low coefficient of friction. This embodiment includes the steps of: (1) preparing a stock suspension of cellulosic fibers, (2) adding a first strength agent to the stock suspension, (3) forming the cellulosic fibers into a substantially uniform web and (4) drying the web into paper and applying a solution containing a second strength agent and a hydrophobic organo-silicone compound to the surface of the paper.

[0053] Preferred hydrophobic organo-silicones are described in U.S. Pat. No. 3,389,042, the disclosure of which is hereby incorporated by reference in its entirety. Commercially available silicones that are especially preferred for use in the present invention are RE-29, GE-OSI and SM-8715 available from Dow Corning Corp. (Midland, Mich.). The hydrophobic organo-silicone is preferably added in solution with the anionic dry-strength agent that is fed into the waterbox. Previously, due to the high cost of silicone, surface sizing was done prior to a silicone coating, and its use as a sizing agent was deterred by its cost (Duraismwamy, C, et al., "Effect of Starch Type on the Silicone Hold-Out of Release Papers, 2000 Coating Conference Proceedings", *TAPPI Journal*, 2001, Vol. 84(3)). However, it has been found that addition of silicone in combination with an anionic dry-strength agent in the waterbox creates a synergistic effect, wherein the silicone imparts some sizing while the dry-strength agent enhances the strength of the surface of the paper product. Of course, silicone sizing agents also can be added in any conventional manner during the papermaking process.

[0054] The hydrophobic organo-silicone is preferably added in an amount of from about 1 lb/ton (0.5 kg/t) to about 10 lb/ton (4.5 kg/t), and more preferably from about 1 lb/ton (0.5 kg/t) to about 5 lb/ton (2.3 kg/t), and most preferably from about 1 lb/ton to about 3 lb/ton (0.5-1.5 kg/t).

[0055] Another particular embodiment of the inventive process yields a paper with a bright surface. Surfaces with an L* value of 89 or above can be obtained. This embodiment includes the steps of: (1) preparing a stock suspension of cellulosic fibers, (2) adding a first strength agent to the stock suspension, (3) forming the cellulosic fibers into a substantially uniform web and (4) drying the web into paper and applying a solution containing a second strength agent and a brightener to the surface of the paper. Compounds useful as brightening agents in practice of the present invention include but are not limited to azoles; biphenyls; chelating agents such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA) and nitrilotriacetic acid (NTA) and other compounds that are capable of chelating heavy metals that catalyze color-form-

ing reactions. Useful optical brighteners further include coumarins; furans; ionic brighteners, including anionic, cationic, and anionic (neutral) compounds, such as the Eccobrite® and Eccowhite® compounds available from Eastern Color & Chemical Co. (Providence, R.I.); naphthalimides; pyrazenes; stilbenes, such as the Leucophor® range of optical brighteners available from the Clariant Corporation (Muttenz, Switzerland), and Tinopal® from Ciba Specialty Chemicals (Basel, Switzerland); salts of such compounds including but not limited to alkali metal salts, alkali earth metal salts, transition metal salts, organic salts (e.g., cyclohexyl and citric acid salts), and ammonium salts of such brightening agents; and combinations of one or more of the foregoing agents.

[0056] Preferably, the brightening agent is added to the paper in an amount of from about 0.01 wt. % to about 90 wt. %. More preferably, paper contains from about 0.1 wt. % to about 50 wt. % brightening agent. For example, the optical brightener can be added in an amount of from about 0.1 lbs/1000 sq. ft of paper to about 0.5 lbs/1000 sq. ft of paper. In accordance with this particular embodiment of the inventive process, the brightener is added to the solution of the second strength agent and applied simultaneously therewith to the paper during the dry stage of the papermaking process. Of course, brightening agents also can be added in any conventional manner during the papermaking process.

[0057] The paper and paper products manufactured according to the inventive process can also optionally contain other additives useful in improving one or more properties of the finished paper product, assisting in the process of manufacturing the paper itself, or both. These additives are generally characterized as either functional additives or control additives.

[0058] Functional additives are typically those additives that are used to improve or impart certain specifically desired properties to the final paper product and include but are not limited to brightening agents, dyes, fillers, sizing agents, starches, and adhesives. Control additives, on the other hand, are additives incorporated during the process of manufacturing the paper so as to improve the overall process without significantly affecting the physical properties of the paper. Control additives include biocides, retention aids, defoamers, pH control agents, pitch control agents, and drainage aids. Paper and paper products made using the process of the present invention may contain one or more functional additive and/or control additive.

[0059] Pigments and dyes impart color to paper. Dyes include organic compounds having conjugated double bond systems; azo compounds; metallic azo compounds; anthraquinones; triaryl compounds, such as triarylmethane; quinoline and related compounds; acidic dyes (anionic organic dyes containing sulfonate groups, used with organic cations such as alum); basic dyes (cationic organic dyes containing amine functional groups); and direct dyes (acid-type dyes having high molecular weights and a specific, direct affinity for cellulose); as well as combinations of the above-listed suitable dye compounds. Pigments are finely divided mineral that can be either white or colored. The pigments that are most commonly used in the papermaking industry are clay, calcium carbonate and titanium dioxide.

[0060] Fillers, are added to paper to increase opacity and brightness. Fillers include but are not limited to calcium

carbonate (calcite); precipitated calcium carbonate (PCC); calcium sulfate (including the various hydrated forms); calcium aluminate; zinc oxides; magnesium silicates, such as talc; titanium dioxide (TiO_2), such as anatase or rutile; clay, or kaolin, consisting of hydrated SiO_2 and Al_2O_3 ; synthetic clay; mica; vermiculite; inorganic aggregates; perlite; sand; gravel; sandstone; glass beads; aeorgels; xerogels; seagel; fly ash; alumina; microspheres; hollow glass spheres; porous ceramic spheres; cork; seeds; lightweight polymers; xonotlite (a crystalline calcium silicate gel); pumice; exfoliated rock; waste concrete products; partially hydrated or unhydrated hydraulic cement particles; and diatomaceous earth, as well as combinations of such compounds.

[0061] The average diameter of the filler particles is typically less than about 5 microns, although sizes up to 200 microns can be used depending upon the thickness of the finished paper sheet. Generally, however, the average particle size diameter of the filler particles is typically from about 0.001 microns to about 100 microns, and more typically from about 0.01 microns to about 50 microns in diameter.

[0062] Fillers are typically added to the pulp suspension in amounts of from about 1 wt. % to about 70 wt. %, and more typically from about 5 wt. % to about 40 wt. %, and most typically from about 10 wt. % to about 30 wt. %, based on total dry weight of the starting pulp stock.

[0063] Fillers typically have an index of refraction from about 1.50 to about 3.00, and more typically from about 1.53 to about 2.80. Indices of refraction of fillers include about 1.50, about 1.51, about 1.52, about 1.53, about 1.54, about 1.55, about 1.56, about 1.57, about 1.58, about 1.59, about 1.60, about 1.61, about 1.62, about 1.63, about 1.64, about 1.65, about 1.70, about 1.75, about 1.80, about 1.90, about 2.00, about 2.10, about 2.20, about 2.30, about 2.40, about 2.50, about 2.60, about 2.70, about 2.80, about 2.90, about 3.00, and ranges between any two of these values.

[0064] Fillers typically have a specific gravity of from about 1.50 to about 4.5, and more typically from about 1.50 to about 4.2, and most typically from about 2.50 to about 2.70.

[0065] Sizing agents are added to the paper during the manufacturing process to aid in the development of a resistance to penetration of liquids through the paper. Sizing agents can be internal sizing agents or external (surface) sizing agents, and can be used for hard-sizing, slack-sizing, or both methods of sizing. More specifically, sizing agents include rosin; rosin precipitated with alum ($\text{Al}_2(\text{SO}_4)_3$); abietic acid and abietic acid homologues such as neoabietic acid and levopimaric acid; stearic acid and stearic acid derivatives; ammonium zirconium carbonate; silicone and silicone-containing compounds, such as RE-29 available from GE-OSI and SM-8715, available from Dow Corning Corporation (Midland, Mich.); fluorochemicals of the general structure $\text{CF}_3(\text{CF}_2)_n\text{R}$, wherein R is anionic, cationic or another functional group, such as Gortex™; alkylketene dimer (AKD), such as Aquapel® 364, Aquapel® 752, Hercon® 70, Hercon® 79, Precis® 787, Precis® 2000, and Precis® 3000, all of which are commercially available from Hercules, Incorporated (Wilmington, Del.); and alkyl succinic anhydride (ASA); emulsions of ASA or AKD with cationic starch; ASA incorporating alum; starch; hydroxymethyl starch; carboxymethylcellulose (CMC); polyvinyl

alcohol; methyl cellulose; alginates; waxes; wax emulsions; and combinations of such sizing agents.

[0066] Starch has many uses in papermaking. For example, it functions as a retention agent, dry-strength agent, surface sizing agent. Starches include but are not limited to amylose; amylopectin; starches containing various amounts of amylose and amylopectin, such as 25% amylose and 75% amylopectin (corn starch) and 20% amylose and 80% amylopectin (potato starch); enzymatically treated starches; hydrolyzed starches; heated starches, also known in the art as "pasted starches"; cationic starches, such as those resulting from the reaction of a starch with a tertiary amine to form a quaternary ammonium salt; anionic starches; ampholytic starches (containing both cationic and anionic functionalities); cellulose and cellulose derived compounds; and combinations of these compounds.

[0067] Microorganisms such as bacteria, algae, yeasts, and fungi are a common problem associated with the papermaking process, often occurring around the paper manufacturing machines themselves and producing slimes that can result in pitted paper products, corrosion damage to the machines, or even breaks in the paper web. The growth of microorganism can be inhibited with biocides. Biocides used in papermaking include thiazoles and thiazolidinones such as isothiazolin, 3-chloroisothiazolidinone, 2-methyl-4-isothiazolin-3-one, 5-chloro-4-isothiazolin-3-one, and 1,2-benzisothiazolin-3-one; quaternary ammonium salts containing alkyl, aryl, or heterocyclic substituents; aldehydes capable of acting as crosslinking agents, such as glutaraldehyde, formaldehyde, and acetaldehyde; alcohols and diols such as 2-bromo-2-nitropropane-1,3-diol (NBG 88, available from Nova BioGenetics, Inc., Atlanta, Ga.); amides, and especially halogenated propionamides such as dibromopropionamide (NBG 20, available from Nova Biogenetics, Inc.); carbamates such as monoalkyl carbamates; chlorine compounds, including both inorganic and organic chemicals that either contain chlorine or can split off chlorine and are commonly employed in the paper industry, including but not limited to alkali hypochloride, alkali earth hypochloride, chlorine, and chlorine dioxides; cyanates such as methylene bis-thiocyanate and disodium cyanodithioimido carbonate; gases such as ozone or chlorine which are capable of being bubbled into a slurry of pulp; peroxides such as hydrogen peroxide (e.g. 35% solution); sulfides such as tetramethylthiuram disulfide; salts such as sodium chloride, sodium peroxide, and sodium hydrogen sulfite; sulfones such as phenyl-(2-chloro-2-cyanovinyl)-sulfone and phenyl-(1,2-dichloro-2-cyanovinyl)-sulfone; organic acids such as benzoic acid, ascorbic acid, formic acid, sorbic acid, p-hydroxybenzoic acid, and mixtures thereof; and silicate such as sodium hexafluorosilicate, and mixtures and combinations of the above.

[0068] Biocides are typically added to the stock suspension in an amount ranging from about 0.1 to about 2.0 lbs/ton of paper. Optimal usage will depend upon the process variables of a given papermachine (primarily degree of closure and incoming raw materials).

[0069] Retention and drainage aids affect the amount of pulp that is retained on the wire and hence incorporated into the paper. Retention and drainage aids include polyamines, such as polyethylenimine (PEI) and poly(diallyldimethylammonium chloride (DADMAC)); high molecular weight polyacrylamides (e.g., those with a molecular weight greater

than 500,000); polyethyleneoxide (PEO); starch; gums; alum; aluminum-containing polymers; wood fibers; and dual component systems containing both cationic and anionic agents, such as polyethyleneimine (PEI) and anionic polyacrylamide, or cationic starch or PAM with colloidal silica, as well as combinations of such compounds.

[0070] Defoamers, compounds used to destabilize and break apart existing foams also can be added to the stock suspension, web or paper. Defoamers are typically used to control the foaming that results when air or other entrained gases mixes in with the stock suspension, especially one of the ingredients of the suspension is a surfactant. Defoamers are usually added late in the papermaking process, near to the origination of the foam. Defoamers include but are not limited to aliphatic chemicals such as kerosene; fuel oils; hydrophobic oils, such as vegetable oils; hydrophobic particles such as hydrocarbon or polyethylene waxes; fatty alcohols; fatty acids; fatty esters; hydrophobic silica; ethylenebisstearamide (EBS) suspended in oil, hydrocarbons, or a water emulsion; alkylpolyethers; silicon oils such as polydimethylsiloxanes; oligomers of ethylene oxide or polypropylene oxide attached to an alcohol, amine, or organic acid, the oligomer having a degree of polymerization from about 3 to about 8; as well as combinations of these compounds. Typically such defoamers are added in an amount of from about 0.01 wt. % to about 1.0 wt. %, and more typically from about 0.01 wt. % to about 0.5 wt. %, based upon total weight of the pulp mixture.

[0071] Additives for the control of pH can also be optionally added to the pulp suspension so as to buffer the overall pH and thereby reduce corrosion of the machines and minimize fungal and bacteria growth. Typical pH control agents include sulfuric acid, carbon dioxide gas bubbled into the slurry, organic buffering agents, and combinations thereof.

[0072] Formation aids promote the dispersion of fibers throughout the slurry. The addition of such compounds can lead to improvements in product formation, as well as improved headbox consistencies. Formation aids include linear, water soluble polyelectrolytes of high molecular weight, such as anionic polyacrylamides; and natural gums such as locust bean gum, karaya gum, and guar gum, as well as mixtures and combinations thereof. These formation aids are typically used at a volume of from about 1 lb/ton (0.5 kg/t) of stock suspension solution to about 10 lb/ton (4.5 kg/t), and more preferably from about 2 lb/ton (0.9 kg/t) to about 6 lb/ton (2.7 kg/t).

[0073] Having thus described the present invention with reference to certain preferred embodiments, it is further illustrated by the examples which follow. These examples are provided for illustrative purposes only and are not intended to limit in any way the invention which is defined by the claims which follow the examples.

EXAMPLES

[0074] The abrasion resistance, indentation resistance, and impact resistance of the paper product produced by the processes of the present invention can be determined by methods and modifications of methods used in such standard industry tests as ASTM D 4977-98b (Standard Test Method for Granule Adhesion to Mineral Surfaced Roofing by Abrasion), ASTM D 5420 (Impact Resistance of Flat, Rigid

Plastic Specimen by Means of a Striker by a Falling Weight (Gardner Impact), or other suitable abrasion or impact tests.

Example 1

[0075] A stock suspension for the outer liner plies of the paper was prepared from recycled wastepaper. The grades of waste paper were flyleaf, sections, and envelope cuttings. This stock suspension was pumped from the machine chest to the fan pump. A metering pump accurately fed the cationic dry-strength agent into a flow of dilution water which was then fed into the liner thick stock prior to the fan pump. The dilution water was used to help mix the dry-strength with the thick stock. The dry-strength agent was fed before the addition of retention aid, ASA, and defoamer.

[0076] The anionic dry-strength agent was blended in a tank with other ingredients (silicone, optical brightener, water). The solution was mixed until all ingredients were thoroughly dispersed. The solution was pumped to a run tank, which feeds to the calender waterbox with the overflow from the waterbox returning to the run tank to maintain a flooded nip.

TABLE 1

Run	Dry-strength Agent Added Prior to Wet end ² (lb/ton)	Dry-strength Agent Added at Dry end ³ (lb/ton)	Abrasion Test Results ⁴	
			Number of Cycles	Caliper Reduction (inches)
control ¹	0	0	200	0.009
1	10.0	6.5	1000	0.001
2	10.0	6.5	1000	0.001
3	10.0	6.5	1000	0.001
4	10.0	6.5	1000	0.002

¹Ordinary gypsum board cover sheet.

²The amount of cationic dry-strength agent added to the stock prior to the wet end of the process.

³The amount of anionic dry-strength agent added to the stock at the dry end of the process.

⁴The abrasion test was performed following generally the procedure of ASTM D4977-98b.

[0077] As can be seen in Table 1, gypsum board facing paper made according to the process of the invention lost only 0.001 to 0.002 inches of surface material after 1000 cycles of abrasion. In contrast, normal gypsum facing paper will lose about 0.009 inches of surface material after only two hundred cycles. Thus, this example illustrates the improvement in surface strength that can be realized with the process.

Example 2

[0078] Paper was produced according to the process described in Example 1, with the addition of an optical brightener, Leucophor® BCW Liquid, T-26 Liquid, or T-4 Liquid (Clariant Corporation, Muttens, Switzerland) to the solution circulating between the run tank and waterbox in the amounts shown in Table 2. Optical brightness was determined using CIE Lab values, as measured on a profilometer wherein L* refers to the value relating to the lightness/darkness of the color; a* refers to the chromaticity on the red/green axis; and b* refers to chromaticity on the blue/yellow axis.

TABLE 2

Example	Quantity of Optical Brightener		L*	b*	a*
	lbs/1000 sq. ft	Gal/batch			
Control	0.0	0.0	87.55	-0.04	3.87
1	0.1	15.0	88.23	-0.08	3.05
2	0.2	30.0	88.57	0.09	2.30
3	0.3	40.0	88.69	-0.02	2.03
4	0.2	30.0	89.37	-0.10	1.81
5	0.2	30.0	89.47	-0.02	1.84
6	0.2	30.0	89.64	-0.01	1.74

[0079] As can be seen in Table 2, the addition of an optical brightener in the waterbox, along with the anionic dry-strength agent yielded a paper product having a marked improvement in optical brightness. While the control paper product contained no optical brightener and had a brightness (L*) of 87.55, the addition of an optical brightener such as Leucophor in the waterbox (e.g., run 6) results in a markedly brighter (L*=89.64, a* ~0 and b* is approaching 0) paper product. That is, L* is approaching 100 (ideal), while a* and b* are both approaching zero, the point of ideal optical brightness (pure white).

[0080] While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and/or processes and in the steps or in the sequence of steps of the methods described herein without departing from the spirit and scope of the invention. More specifically, it will be apparent that certain agents which are chemically related can be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit and scope of the invention.

What is claimed is:

1. A process for making paper and paper products comprising:

- a stock preparation stage wherein a stock suspension of cellulosic fibers is prepared,
- adding a first strength agent selected from the group consisting of cationic dry-strength agents, amphoteric dry-strength agents and cationic wet-strength agents to the stock suspension,
- a wet end stage wherein the cellulosic fibers are formed into a substantially uniform web, and
- a dry end stage wherein the web is dried into paper and a second strength agent selected from the group consisting of anionic dry-strength agents and amphoteric strength agents is applied to the surface of the paper.

2. The process of claim 1 wherein the first strength agent is a cationic dry-strength agent.

3. The process of claim 2 wherein the cationic dry-strength agent is selected from the group consisting of cationic polyacrylamides, cationic natural polymers, cationic modified natural polymers, cationic synthetic polymers, starches modified to have quaternary ammonium

functional groups, cationic celluloses, cationic natural gums, cationic polyvinyl alcohol adducts, and combinations thereof.

4. The process of claim 3 wherein the cationic dry-strength agent is a cationic polyacrylamide.

5. The process of claim 2 wherein the cationic dry-strength agent is added in an amount of from about 1 lb/t (0.5 kg/t) to about 20 lb/t (9.1 kg/t).

6. The process of claim 2 wherein the cationic dry-strength agent has a viscosity from about 1,000 cps (1 Pa-s) to about 15,000 cps (15 Pa-s).

7. The process of claim 2 wherein the cationic dry-strength agent has a specific gravity of from about 1.00 to about 1.20.

8. The process of claim 1 wherein the first strength agent is a cationic wet-strength agent.

9. The process of claim 8 wherein the cationic wet-strength agent is selected from the group consisting of cationic acid curing resins, cationic neutral to acid curing resins, and cationic neutral to alkaline curing resins.

10. The process of claim 8 wherein the cationic wet-strength agent is added in an amount of from about 1 lb/t (0.5 kg/t) to about 20 lb/t (9.1 kg/t).

11. The process of claim 1 wherein the second strength agent is an anionic dry-strength agent.

12. The process of claim 11 wherein the anionic dry-strength agent is selected from the group consisting of anionic polyacrylamides, anionic natural starches, and anionic carboxymethylcellulose.

13. The process of claim 12 wherein the anionic dry-strength agent is an anionic polyacrylamide.

14. The process of claim 11 wherein the anionic dry-strength agent is added in an amount of from about 5 lbs/t (2.3 kg/t) to about 25 lbs/t (11.3 kg/t).

15. The process of claim 11 wherein the anionic dry-strength agent has a specific gravity from about 1.00 to about 1.20.

16. The process of claim 11 wherein the anionic dry-strength agent has a viscosity from about 1,000 cps (1 Pa-s) to about 15,000 cps (15 Pa-s).

17. The process of claim 1 wherein the second strength agent is applied to the surface of the paper by a technique selected from the group consisting of:

- immersing the paper in a solution of the second strength agent in a calender waterbox,
- applying a solution of the second strength agent to the paper with a size press, and
- spraying a solution of the second strength agent on the paper using a sprayboom.

18. The process of claim 17 wherein the solution of the second dry-strength agent is applied to the paper in a calender waterbox.

19. The process of claim 17 wherein the solution further contains at least one optical brightener.

20. The process of claim 19 wherein the at least one optical brightener is selected from the group consisting of azoles, biphenyls, chelating agents, coumarins, furans, ionic brighteners, naphthalimides, pyrazenes, stilbenes, tetrasulfonated stilbenes, hexasulfonated stilbenes, salts thereof, and combinations thereof.

21. The process of claim 19 wherein the at least one optical brightener is added in an amount of from about 0.1 lbs/MSF to about 0.5 lbs/1000 square feed.

22. The process of claim 19 wherein the paper product has an optical brightness with a lightness value, L^* , greater than about 0.89 after application of the solution.

23. The process of claim 1 further comprising adding at least one biocide to the stock suspension.

24. The process of claim 17 wherein the solution further contains at least one hydrophobic organo-silicone.

25. Paper made by the process of claim 1.

26. The process of claim 1 further comprising incorporating the paper into a paper product.

27. A paper product made by the process of claim 26.

28. A paper product of claim 27 that is drywall (wallboard) facing paper applied to the drywall by a conventional gypsum wallboard industry manufacturing process or by lamination onto the drywall after it is manufactured.

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