

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 November 2006 (30.11.2006)

PCT

(10) International Publication Number
WO 2006/127050 A1

(51) International Patent Classification:
D21H 21/10 (2006.01)

(21) International Application Number:
PCT/US2005/046946

(22) International Filing Date:
23 December 2005 (23.12.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/684,816 26 May 2005 (26.05.2005) US
11/313,504 21 December 2005 (21.12.2005) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 2006/127050 A1

(54) Title: HYDROPHOBIC POLYMERS AND THEIR USE IN PREPARING CELLULOSIC FIBER COMPOSITIONS

(57) Abstract: A method of improving retention and drainage comprising adding a water compatible hydrophobic copolymer to a papermaking slurry is disclosed. A composition comprising a water compatible hydrophobic copolymer is described.

HYDROPHOBIC POLYMERS AND THEIR USE IN PREPARING CELLULOSIC FIBER COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/684,816, filed May 26, 2005, the entire content of which is herein incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to the use of hydrophobic polymers and copolymers in the preparation of cellulosic fiber compositions. The present invention further relates to cellulosic fiber compositions, such as paper and paperboard, which incorporate the water compatible hydrophobic polymers or copolymers.

BACKGROUND OF THE INVENTION

[0003] The making of cellulosic fiber sheets, particularly paper and paperboard, includes the following: 1) producing an aqueous slurry of cellulosic fiber; which may also contain inorganic mineral extenders or pigments; 2) depositing this slurry on a moving papermaking wire or fabric; and 3) forming a sheet from the solid components of the slurry by draining the water.

[0004] The foregoing is followed by pressing and drying the sheet to further remove water. Organic and inorganic chemicals are often added to the slurry prior to the sheet-forming step to make the papermaking method less costly, more rapid, and/or to attain specific properties in the final paper product.

[0005] The paper industry continuously strives to improve paper quality, increase productivity, and reduce manufacturing costs. Chemicals are often added to the fibrous slurry before it reaches the papermaking wire or fabric, to improve the

method drainage/dewatering and solids retention; these chemicals are called retention and/or drainage aids.

[0006] As to drainage/dewatering improvement, drainage or dewatering of the fibrous slurry on the papermaking wire or fabric is often the limiting step in achieving faster machine speeds. Improved dewatering can also result in a drier sheet in the press and dryer sections, resulting in reduced steam consumption. In addition, drainage and dewatering is the stage in the papermaking process that determines many final sheet properties.

[0007] With respect to solids retention, papermaking retention aids are used to increase the retention of fine furnish solids in the web during the turbulent method of draining and forming the paper web. Without adequate retention of the fine solids, they are either lost to the mill effluent or accumulate to high levels in the recirculating white water loop, potentially causing deposit buildup. Additionally, insufficient retention increases the papermakers' cost due to loss of additives intended to be adsorbed on the fiber to provide paper opacity, strength, or sizing properties.

[0008] High molecular weight (MW) water-soluble polymers with either cationic or anionic charge have traditionally been used as retention and drainage aids. Recent developments of inorganic microparticles in combination with high MW water-soluble polymers have shown superior retention and drainage efficacy compared to conventional high MW water-soluble polymers. U.S. Patent Nos. 4,294,885 and 4,388,150 teach the use of starch polymers with colloidal silica. U.S. Patent No. 4,753,710 teaches flocculating the pulp furnish with a high MW cationic flocculant, inducing shear to the flocculated furnish, and then introducing bentonite clay to the furnish. U.S. Patent Nos. 5,274,055 and 5,167,766 disclose using chemically cross-linked organic microparticles or micropolymers as retention and drainage aids in the papermaking process.

[0009] Copolymers are also used to control deposition of contaminants or organic deposits in papermaking systems. Organic deposit(s) is a term used to describe tacky, water insoluble materials in the papermaking system that are detrimental to the production of paper. Such materials derived from trees during the

pulping and papermaking process are termed pitch or wood pitch, while the term stickies is used to describe contaminants that are derived from adhesives introduced into the papermaking process as a contaminant of recycled fiber. One strategy for eliminating these materials is to agglomerate the organic deposits into larger, non-tacky particles that can be removed from the papermaking stock or incorporated into the sheet without causing deposits in the papermaking system or defects in the sheet. Chemicals that are able to interact with organic deposits and mitigate their negative impact include surfactants and polymers. The polymers can be ionic or nonionic, and includes materials used as flocculants, coagulants and dispersants.

[0010] The efficacy of the polymers or copolymers used will vary depending upon the type of monomers from which they are composed, the arrangement of the monomers in the polymer matrix, the molecular weight of the synthesized molecule, and the method of preparation.

[0011] It has been found, unexpectedly, that hydrophobic polymers or copolymers provide unanticipated retention and drainage activity and can function as contaminant control aids in applications including papermaking applications. Although the synthesis methods employed are generally known to those skilled in the art, there is no prior art suggesting that the unique physical characteristics would result in the unanticipated activity observed.

SUMMARY OF THE INVENTION

[0012] The present invention is directed to water compatible hydrophobic polymers and copolymers and cellulosic fiber compositions containing the hydrophobic polymers and copolymers, particularly a cellulosic sheet such as paper or paperboard. The invention is also directed to a method for making the hydrophobic polymers and copolymers and the cellulosic fiber compositions.

[0013] In another aspect, the present invention provides a method of making a cellulosic fiber composition comprising adding, to a cellulosic pulp slurry, a water compatible polymer or copolymer that contains a hydrophobic group.

[0014] The invention further relates to cellulosic fiber compositions, including an aqueous slurry of cellulosic pulp, containing such water compatible polymers and copolymers. As used herein, the term copolymer is understood to be polymer compositions consisting of two or more different monomeric units.

[0015] Additionally, a composition comprising water compatible hydrophobic polymers and copolymers and cellulose fibers and optionally, a siliceous material is disclosed.

[0016] In accordance with the present invention, it has been unexpectedly discovered that certain water compatible hydrophobic polymers and copolymers exhibit unique physical characteristics and provide unanticipated activity as retention and drainage aids.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention provides for enhanced retention and/or drainage in a papermaking process by addition of a water compatible hydrophobic polymer or copolymer to a papermaking slurry.

[0018] The present invention also provides for a composition comprising a water compatible hydrophobic polymer or copolymer and cellulose fiber.

[0019] The present invention also provides for a composition comprising a hydrophobic polymer or copolymer, a siliceous material and cellulose fibers.

[0020] The present invention also provides for the use of water compatible polymer(s) and copolymer(s) that interact or associate, via non covalent bonding to form an aggregation of two or more polymer chains. The driving force for the molecular association can be electrostatic or hydrophobic in nature. Preferred are molecular associations driven by hydrophobic forces.

[0021] The use of multi-component systems in the manufacturing of paper and paperboard provides the opportunity to enhance performance by utilizing materials that have different effects on the process and/or product.

[0022] The polymer is described to be water compatible. For the purposes of the present invention, "water compatible" means that the polymer can be water soluble or water swellable or water dispersible.

[0023] The term water soluble is used to indicate that the polymer will dissolve in the solvent, with no visible solid material remaining in the solvent. Solubility of a polymer in a solvent occurs when the free energy of mixing is negative. Examples of water soluble materials include, but are not limited to, exudates or gum, extractives, natural materials, modified natural materials, or synthetic material. One example of exudates or gum is gum tragacanth. One example of extractives is pectin. One example of natural materials is guar. One example of modified natural materials is derivatized cellulose such as methylcellulose. One example of synthetic material is poly(acrylic acid). The synthetic polymers can be comprised of one or more monomers selected to provide specific properties to the final polymer.

[0024] Water swellable polymers are those that can imbibe the aqueous solvent and swell to a limited extent. Water swellability can be influenced by a number of factors including, but not limited to, crosslinking and electrostatic interactions. Thus, the interactions between polymer and solvent are limited. Although a visible homogeneous solution may be obtained, it is not a uniform molecular dispersion. One example of a water swellable polymer is a crosslinked polymer. Cross linked polymers can be water compatible and water dispersible. In contrast, a branched polymer can be soluble.

[0025] Water dispersible materials are those that are not soluble in water, but do not phase separate. Typically, these materials have a modified surface that allows them to remain as discrete particulate material that is suspended in water, or can be made dispersible by the addition of other materials. Examples include latex particle, oil-in-water emulsions, and dispersed clays or pigments.

[0026] Hydrophobic substances are generally defined as substances that are readily soluble in many nonpolar solvents, but are incapable of completely dissolving in water. Hydrophobic materials resist association with water and tend to cluster together in aqueous environment. A hydrophilic material, in contrast, is soluble in water, but only sparingly soluble in most nonpolar solvents. Hydrophilic materials are hydrated by water, resulting in solutions of the hydrophilic material in water.

[0027] An amphiphilic compound is one that has both a hydrophobic and hydrophilic segment. Thus, it is comprised of both a polar water soluble group (hydrophilic segment) and a nonpolar water insoluble group (hydrophobic segment). For example, a surfactant is an amphiphilic compound. The amphiphilic nature of the materials are such that they will migrate to interfaces, be it liquid/gas, liquid/liquid or liquid/solid.

[0028] The hydrophobic polymers of the present invention are amphiphilic in nature in that they have regions that are more hydrophobic in nature and regions that are more hydrophilic in nature. The relative extent of hydrophobicity and hydrophilicity will determine the solubility of the material. In practice, the materials that are, overall, more hydrophobic will be relatively more water insoluble and oil soluble. Conversely, the more hydrophilic materials will be relatively more water soluble and oil insoluble.

[0029] Polymers useful in the present invention are typically copolymers. The term copolymer is understood to be a polymeric molecule that contains two or more different monomers. They can be copolymers of more than one monomer or polymers where a fraction of the monomers are chemically derivatized.

[0030] A hydrophobic monomer is, as defined here, an amphiphilic compound. A segment of the molecule is hydrophobic. Hydrophobicity is a relative property. For example, an ethylenically unsaturated monomer can be water soluble. Examples are acrylamide and acrylic acid. Modification can make the monomer more hydrophobic. Methacrylamide and methacrylic acid are less water soluble due to the methyl group. Ethyl acrylate would be even less soluble as it has a larger

hydrophobic group. Butyl acrylate, by virtue of its even larger alkyl chain, is even more hydrophobic.

[0031] Materials having utility in the present invention are known in the art by a number of terms including, but not limited to, hydrophobic polymers, amphiphilic polymers, hydrophobically modified polymer, and polymeric surfactants.

[0032] These materials can be made by a number of processes, including, but not limited to, synthesis of polymers from one or more monomers, derivatization of existing polymer or grafting; grafting can occur either concurrent with or subsequent to polymerization.

[0033] A hydrophobic polymer of utility in the present invention is a copolymer wherein at least one of the monomers is hydrophobic in nature. The hydrophobic monomer is, on a molar basis, less than 50% of the monomers, preferably less than 10%, more preferably less than 5% and most preferably less than 2%.

[0034] Hydrophobic polymers, more commonly referred to as hydrophobically modified polymers, are water compatible polymers onto which hydrophobic groups are chemically attached, either at the ends of the chain (telechelic or end-capped) or randomly along the polymer chain (comb-like or pendant). A polymer with hydrophobic group can undergo intermolecular association with another chain, forming a network mediated by self-association of the hydrophobes. That this association occurs without the formation of covalent bonds is an important facet of the invention. This network formation results in, amongst other unique properties, a strong viscosifying or thickening effect. A molecule with at least two hydrophobes on a single chain can also undergo intra-molecular association, altering the structure of the molecule in solution and hence, its viscosity.

[0035] Associative forces between hydrophobic groups occur due to the well known phenomenon that is termed "the hydrophobic effect". Hydrophobic substances are materials that are soluble in many nonpolar solvents, but can be sparingly soluble in water. There is an attraction between hydrophobic materials (i.e., oil) and water; this is, however, not nearly as strong as the attraction that water

has for itself. Hydrogen bonding between water molecules induces segregation of hydrophobic materials, effectively resulting in hydrophobe-hydrophobe association. This water-induced attraction is termed a hydrophobic interaction. Thus, the hydrophobic effect occurs only in an aqueous environment.

[0036] The assembly of hydrophobic molecules requires the removal of water from the regions between them. Thus, association of polymer bound hydrophobes results in a region not solvated by water molecules. In an aqueous solution, these aggregates are not free draining and can act as small water insoluble (particulate) regions. Without being bound by theory, it is believed that this is the mechanism by which the polymers of the present invention provide their performance properties.

[0037] One approach to producing a hydrophobic polymer is by direct polymerization of monomers, which includes a least one hydrophobic monomer, to form a copolymer. Polymerization may be done by any method known in the art, including solution, dispersion and inverse emulsion polymerization.

[0038] The polymers can comprise, in addition to the hydrophobic monomers, one or more anionic, cationic and/or nonionic monomers. The anionic, cationic and nonionic monomers can be used at any desired ratio. The polymer can contain 0 to 80% anionic monomers, 0 to 80% cationic monomers and 0 to 100% nonionic monomers. Preferred compositions are 0 to 60% anionic monomers, 0 to 30% cationic monomers and about 10 to 100% nonionic monomers.

[0039] Exemplary nonionic monomers include, but are not limited to, acrylamide; methacrylamide; *N*-alkylacrylamides, such as *N*-methylacrylamide; *N,N*-dialkylacrylamides, such as *N,N*-dimethylacrylamide; methyl acrylate; methyl methacrylate; acrylonitrile; *N*-vinyl methylacetamide; *N*-vinyl formamide; *N*-vinyl methyl formamide; vinyl acetate; *N*-vinyl pyrrolidone; alkyl acrylates; alkyl methacrylates; alkyl acryamides; alkyl methacrylamides; and alkyloxylated acrylates and methacrylates such as alkyl polyethyleneglycol acrylates, alkyl polyethyleneglycol methacrylates; mixtures of any of the foregoing and the like.

[0040] Exemplary anionic monomers include, but are not limited to, the free acids and salts of acrylic acid; methacrylic acid; maleic acid; itaconic acid; acrylamidoglycolic acid; 2-acrylamido-2-methyl-1-propanesulfonic acid; 3-allyloxy-2-hydroxy-1-propanesulfonic acid; styrenesulfonic acid; vinylsulfonic acid; vinylphosphonic acid; 2-acrylamido-2-methylpropane phosphonic acid; mixtures of any of the foregoing and the like.

[0041] Exemplary cationic monomers include, but are not limited to, the free bases and salts of cationic ethylenically unsaturated monomers such as the diallyldialkylammonium halides, such as diallyldimethylammonium chloride; the (meth)acrylates of dialkylaminoalkyl compounds, such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth) acrylate, dimethyl aminopropyl (meth)acrylate, 2-hydroxydimethyl aminopropyl (meth)acrylate, aminoethyl (meth)acrylate, and the salts and quaternaries thereof; the *N,N*-dialkylaminoalkyl(meth)acrylamides, such as *N,N*-dimethylaminoethylacrylamide, and the salt and quaternaries thereof and mixture of the foregoing and the like.

[0042] The hydrophobic monomer can be any monomer that has a hydrophobic moiety as an integral part of its structure. The hydrophobic moiety may be linear or cyclic, aliphatic or aromatic. Preferred hydrophobic moieties are typically alkyl groups such as, but not limited to, propyl, butyl, hexyl, octyl, decyl, dodecyl (lauryl), cetyl, stearyl and behenyl groups.

[0043] Exemplary hydrophobic monomers include, but are not limited to, ethylenically unsaturated monomers having hydrophobic moieties. The hydrophobic groups include hydrophobic organic groups, such as those having hydrophobicity comparable to one of the following: aliphatic hydrocarbon groups having at least six carbons (preferably from C₈ to C₂₂ alkyls and preferably from C₆ to C₂₂ cycloalkyls); poly-nuclear aromatic hydrocarbon groups such as benzyls, substituted benzyls and naphthyls; alkaryl groups wherein alkyl has one or more carbons; haloalkyls of four or more carbons, preferably perfluoroalkyls; polyalkyleneoxy groups wherein the alkylene is propylene or higher alkylene and there is at least one alkyleneoxy unit per hydrophobic moiety. The preferred hydrophobic groups include those having at least 3 carbons or more per hydrocarbon group, preferably at least 6 carbons or more.

Also preferred are those hydrophobic groups having C₆ to C₂₂ alkyl groups or those having at least 6 carbons or more per perfluorocarbon group, such as the C₆F₁₃ – C₂₂F₄₅. Particularly preferred are the C₈ – C₂₀ alkyl groups.

[0044] Suitable hydrocarbon groups containing ethylenically unsaturated monomers include the esters of amides of the C₆ and larger alkyl groups. Particularly suitable esters include, but are not limited to, dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, nonyl-*alpha*-phenyl acrylate, nonyl-*alpha*-phenyl methacrylate, dodecyl-*alpha*-phenyl acrylate, and dodecyl-*alpha*-phenyl methacrylate. The C₁₀ – C₂₀ alkyl esters of acrylic and methacrylic acid are preferred. Of these, dodecyl acrylate and methacrylate are particularly preferred.

[0045] Also the following hydrocarbon group-containing ethylenically unsaturated monomers may be used: *N*-alkyl ethylenically unsaturated amides, such as *N*-octadecyl acrylamide, *N*-octadecyl methacrylamide, *N*-octyl acrylamide, *N,N*-dioctyl acrylamide and similar derivatives thereof; *alpha*-olefins, such as 1-octene, 1-decene, 1-dodecene, and 1-hexadecene; vinyl alkylates wherein the alkyl has at least eight carbons, such as vinyl laurate and vinyl stearate; vinyl alkyl ethers, such as dodecyl vinyl ether and hexa-vinyl alkyl ethers, such as dodecyl vinyl ether and hexa-decyl vinyl ether; *N*-vinyl amides, such as *N*-vinyl lauramide and *N*-vinyl stearamide.

[0046] The hydrophobic monomer is present in the hydrophobic copolymer in an amount up to about 10 mole percent, preferably up to 5 mole percent and even more preferably up to 2 mole percent. It is preferred that the hydrophobic monomer be present in an amount from at least about 0.01, preferably at least 0.1 mole percent. It is preferred that the hydrophobic monomer be present in an amount from about 0.01 to about 2 mole percent and most preferred that the hydrophobic monomer be present in an amount from about 0.1 to about 1 mole percent. Preferred hydrophobic monomers are octylacrylamide and lauryl acrylate.

[0047] The molar ratio of the hydrophobic, anionic, cationic and nonionic monomer can be varied to contain any relative amount of the monomers necessary to achieve the desired solubility.

[0048] Preferably the water compatible hydrophobic polymers and copolymers useful in the present invention are prepared by an inverse (water-in-oil) emulsion polymerization technique. Such processes are known to those skilled in the art, for example see U.S. Pat. No. 3,284,393, and Reissue U.S. Pat. Nos. 28,474 and 28,576, the entire contents of each is herein incorporated by reference. Preparation of an aqueous solution from the emulsion polymer may be affected by inversion by adding the emulsion polymer to water, wherein the emulsion or water may also contain a breaker surfactant. Breaker surfactants are additional surfactants that are added to a polymer emulsion to promote inversion. The resulting copolymers may also be further isolated by precipitating in an organic solvent such as acetone and dried to a powder form. The powder can be easily dissolved in an aqueous medium for use in desired applications.

[0049] In general, an inverse emulsion polymerization process is conducted by 1) preparing an aqueous solution of the monomers, 2) adding the aqueous solution to a hydrocarbon liquid containing appropriate surfactant or surfactant mixture to form an inverse monomer emulsion, 3) subjecting the monomer emulsion to free radical polymerization, and 4) optionally adding a breaker surfactant to promote the inversion of the emulsion when added to water.

[0050] Polymerization of the emulsion may be carried out in any manner known to those skilled in the art. Initiation may be effected with a variety of thermal and redox free-radical initiators including, but not limited to, azo compounds such as azobisisobutyronitrile and the like. Polymerization may also be effected by photochemical irradiation processes, irradiation or by ionizing radiation with a ⁶⁰Co source.

[0051] Preferred initiators are oil soluble thermal initiators. Typical examples include, but are not limited to, 2,2'-azobis-(2,4-dimethylpentanonitrile); 2,2'-

azobisisobutyronitrile (AIBN); 2,2'-azobis-(2-methylbutanonitrile); 1,1'-azobis-(cyclohexanecarbonitrile); benzoyl peroxide and lauroyl peroxide.

[0052] Any chain transfer agents known to those skilled in the art may be used to control the molecular weight. Those include, but are not limited to, lower alkyl alcohols such as isopropanol; amines; mercaptans such as mercaptoethanol, phosphites; thioacids; allyl alcohol; and the like.

[0053] The aqueous solution typically comprises an aqueous mixture of monomers. The aqueous phase may also comprise such conventional additives as are desired. For example, the mixture may contain chelating agents, pH adjusters, initiators, chain transfer agents as described above, and other conventional additives. For the preparation of the water-compatible hydrophobic copolymer, the pH of the aqueous solution is below 12 and is preferably equal to or greater than 2, more preferably the pH is about 4 to about 6.

[0054] The hydrocarbon liquid typically comprises straight-chain hydrocarbons, branched-chain hydrocarbons, saturated cyclic hydrocarbons, aromatic hydrocarbons, or mixtures thereof.

[0055] The surfactants or surfactant mixtures used in the invention are generally oil soluble. One or more surfactants can be used. Exemplary surfactants include, but are not limited to, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, ethylene oxide and/or propylene oxide adducts of long chain fatty acids or alcohols, ethylene oxide and/or propylene oxide adducts of alkyl phenols, alkanolamides, mixed ethylene oxide/propylene oxide block copolymers, diblock and triblock copolymers based on polyester derivatives of fatty acids and poly(ethyleneoxide), diblock and triblock copolymers based on poly(ethyleneoxide) and poly(propyleneoxide), diblock and triblock copolymers based on polyisobutylene succinic anhydride and poly(ethyleneoxide), mixtures of any of the foregoing and the like. Specific surfactants include sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, polyoxyethylene sorbitan monooleate, and surfactants sold by BASF under the Pluronic® trade name and surfactants by Uniqema under the Atlas® and Arlacel® trade names.

[0056] Polymerization of the inverse emulsion may be carried out in any manner known to those skilled in the art, for example see Allcock and Lampe, *Contemporary Polymer Chemistry*, (Englewood Cliffs, New Jersey, PRENTICE-HALL, 1981), chapters 3-5.

[0057] An alternative mechanism to prepare a hydrophobic polymer is grafting. One example is copolymerization of ethylenically unsaturated monomers, such as acrylic acid with block copolymers of ethylene oxide and propylene oxide. Selection of the polymerization conditions will impact the structure of the polymer and, hence, its utility. These polymers, are known in the art, to associate via hydrophobic forces, to form aggregates.

[0058] Exemplary polymers prepared by grafting includes, but are not limited to, polymers with poly(ethylene oxide) (PEO) arms and a core consisting of hydrophobic triisocyanate or tetraisocyanate that were shown to possess associative properties when the PEO arms were modified with hydrophobic nonylphenoxy end groups, hydrophobically modified ethoxylated urethane (HEUR) polymers, fluorocarbon-containing polymers, end capped poly(ethylene oxide) such as hexadecyl-terminated poly(ethylene oxide) and the like and mixtures thereof.

[0059] Yet another material is a graft copolymer of acrylic acid and a monoamino-terminated surfactant. The surfactant is grafted via an amide bond using dicyclocarbodiimide as a coupling agent.

[0060] Yet another method for preparation of hydrophobic water compatible polymer is by derivatizing an existing synthetic polymer. This can be achieved by a number of technical approaches, which include but are not limited to, the grafting of a hydrophobic amine via the Mannich reaction.

[0061] Yet another method for preparation is the use of a water dispersible macromer, sometimes referred to as polymerizable surfactant, such as nonylphenoxy poly(ethylene oxide) acrylate that can be copolymerized with an

ethylenically unsaturated monomer to a self-assembling hydrophobically modified polymer.

[0062] Yet another method for preparation is to modify an already prepared polymeric backbone. This method implies either utilization of an aprotic solvent common for the polymer and a hydrophobic entity to be grafted upon the polymer, or selective hydrophilization of a hydrophobic water insoluble block copolymer.

[0063] Hydrophobically modified alkali-swellaable emulsion, or HASE, are also useful in the present invention. These materials are hydrophobically modified acrylate copolymers. An example would be a copolymer of methacrylic acid, ethylacrylate and a third monomer termed an associative macromonomer. An example of associative macromonomer is an ethylenically unsaturated monomer with a pendant hydrocarbon of more than 6 carbons linked to the monomer by an ethylene oxide chain. Key variables are the chemistry of the hydrocarbon and the length of these ethylene oxide chains.

[0064] Additional polymers useful in the present invention are hydrophobically modified polymers based on natural occurring polymers such as proteins and polysaccharides. Derivatized natural materials, including starch and cellulose derivatives can also be used. Exemplary based polymers include, but are not limited to, hydroxyethyl cellulose and cationic starch. Preferred are nonionic water soluble cellulose ether can be used as the cellulose ether substrate used to form the products of this invention. Thus, e.g., hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, ethyl hydroxyethyl cellulose, and methyl hydroxyethyl cellulose can all be modified. The amount of nonionic substituent such as methyl, hydroxyethyl or hydroxypropyl; does not appear to be critical so long as there is sufficient to assure that the ether is water soluble.

[0065] The preferred cellulose ether substrate is hydroxyethyl cellulose (HEC). Accordingly, control of the modification process and control of the properties of the modified product can be more precise with this substrate. Hydrophilicity of the most commonly used nonionic cellulose ethers varies in the general direction: hydroxyethyl>hydroxypropyl>hydroxypropyl>methyl.

[0066] Long chain alkyl modifier can be attached to the cellulose ether substrate via an ether, ester or urethane linkage. Preferred is the ether linkage as the reagents most commonly used to effect etherification are readily obtained, the reaction is similar to that commonly used for the initial etherification, and the reagents are usually more easily handled than the reagents employed for modification via the other linkages. The resulting linkage is also usually more resistant to further reactions.

[0067] Methods of preparing mixed ethers of cellulose, i.e., products having more than one etherifying modifier attached to the same cellulose molecule are known to the art. The products of this invention can be prepared via essentially the same methods. Briefly, the preferred procedure for preparing the mixed ethers of this invention comprises slurring the nonionic cellulose ether in an inert organic diluent such as a lower aliphatic alcohol, ketone, or hydrocarbon and adding a solution of alkali metal hydroxide to the resultant slurry at a low temperature. When the ether is thoroughly wetted and swollen by the alkali, a C₁₀ to C₂₄ epoxide is added and the reaction is continued, with agitation, until complete. Residual alkali is then neutralized and the product is recovered, washed with inert diluents, and dried. The etherification can also be effected with a C₁₀ to C₂₄ halide or halohydrate but these are sometimes less reactive, less efficient and more corrosive so it is preferred to use epoxide.

[0068] Substantially the same procedure is used to attach the hydrocarbon modifier via the ester or urethane linkage. Conventional slurry methods of reacting this type of modifier with cellulose ethers, i.e., without the alkali, are ineffective. The alkali step is required in order to assure that the cellulose ether is swollen to the point that the modifier can react substantially uniformly on all cellulose ether molecules throughout. If reaction is not substantially uniform throughout the cellulose ether mass, the improved performance properties are not realized.

[0069] Optionally, siliceous materials can be used as an additional component of a retention and drainage aid used in making paper and paperboard. The siliceous material may be any of the materials selected from the group consisting of silica

based particles, silica microgels, amorphous silica, colloidal silica, anionic colloidal silica, silica sols, silica gels, polysilicates, polysilicic acid, and the like. These materials are characterized by the high surface area, high charge density and submicron particle size.

[0070] This group includes stable colloidal dispersion of spherical amorphous silica particles, referred to in the art as silica sols. The term sol refers to a stable colloidal dispersion of spherical amorphous particles. Silica gels are three dimensional silica aggregate chains, each comprising several amorphous silica sol particles, that can also be used in retention and drainage aid systems; the chains may be linear or branched. Silica sols and gels are prepared by polymerizing monomeric silicic acid into a cyclic structure that result in discrete amorphous silica sols of polysilicic acid. These silica sols can be reacted further to produce a three-dimensional gel network. The various silica particles (sols, gels, etc.) can have an overall size of 5-50 nm. Anionic colloidal silica can also be used.

[0071] The siliceous material can be added to the cellulosic suspension in an amount of at least 0.05 Kg per metric ton based on dry weight of the cellulosic suspension. The amount of siliceous material may be as high as 5 Kg per metric ton. Preferably, the amount of siliceous material is from about 0.05 to about 25 Kg per metric ton. Even more preferably the amount of siliceous material is from about 0.25 to about 5 Kg per metric ton based on the dry weight of the cellulosic suspension.

[0072] The components of a retention and drainage system may be added substantially to the cellulosic suspension. The term retention and drainage system is used here to encompass two or more distinct materials added to the papermaking slurry to provide improved retention and drainage. For instance, the components may be added to the cellulosic suspension separately either at the same stage or dosing point or at different stages or dosing points. When the components of the inventive system are added simultaneously any two or more of the materials may be added as a blend. The mixture may be formed in situ by combining any two or more of the materials at the dosing point or in the feed line to the dosing point. Alternatively the inventive system comprises a preformed blend of the any two or

more of the materials. In an alternative form of the invention the components of the inventive system are added sequentially. A shear point may or may not be present between the addition points of the components. The components can be added in any order.

[0073] The inventive system is typically added to the paper process to affect retention and drainage. The inventive system may be added to the thick stock or thin stock, preferably the thin stock. The system may be added at one feed point, or may be split fed such that the inventive system is fed simultaneously to two or more separate feed points. Typical stock addition points include feed points(s) before the fan pump, after the fan pump and before the pressure screen, or after the pressure screen.

[0074] The amount of siliceous material in relationship to the amount of associative polymer copolymer used in the present invention can be about 100:1 to about 1:100 by weight, or from about 50:1 to 1:50 or about 10:1 to 1:10.

[0075] Yet another additional components that can be part of the inventive system are aluminum sources such as alum (aluminum sulfate), polyaluminum sulfate, polyaluminum chloride and aluminum chlorohydrate.

[0076] The copolymers useful in the invention can be used in papermaking systems and processes. The copolymers are useful as drainage and retention aids as well as contaminant control aids. In commercial papermaking, a slurry of cellulosic fibers or pulp is deposited on a moving papermaking wire or fabric. The slurry may contain other chemicals, such as sizing agents, starches, deposit control agents, mineral extenders, pigments, fillers, organic or inorganic coagulants, conventional flocculants, or other common additives to paper pulp. As water from the deposited slurry is removed, a sheet forms. Ordinarily the sheets are then pressed and dried to form paper or paper board. The copolymers of the invention are added to the slurry before it reaches the wire to improve the drainage or dewatering and the retention of the fiber fines and fillers in the slurry.

[0077] As a contaminant control aid, the polymers of the present invention inhibit the deposition of pitch and stickies from the virgin or recycled pulp stock on the papermaking equipment. The aid is added to the pulp slurry where it interferes with the agglomeration of the pitch and stickies that would otherwise detrimentally affect the paper, paper making equipment or paper making processes. A method of inhibiting deposition of pitch and stickies comprises adding a hydrophobic polymer to a cellulosic pulp slurry.

[0078] Suitable cellulosic fiber pulps for the method of the invention include conventional papermaking stock such as traditional chemical pulp. For instance, bleached and unbleached sulfate pulp and sulfite pulp, mechanical pulp such as groundwood, thermomechanical pulp, chemi-thermomechanical pulp, recycled pulp such as old corrugated containers, newsprint, office waste, magazine paper and other non-deinked waste, deinked waste, and mixtures thereof, may be used.

[0079] The copolymers useful in the invention may be provided to the end use application in a number of physical forms. In addition to the original emulsion form, the inventive copolymer may also be provided as an aqueous solution, dry solid powder, or dispersion form.

[0080] The hydrophobic polymer is typically diluted or inverted at the application site to produce an aqueous solution of 0.1 to 1% active polymer. Alternatively, a dried material is dissolved in water to produce an aqueous solution.

[0081] The present invention provides for a method of improving retention and or drainage of a cellulosic pulp slurry wherein the method comprises adding hydrophobic polymer to a cellulosic pulp slurry to improve drainage.

[0082] This dilute solution of the copolymers used in the invention is added to the paper process to affect retention and drainage. The inventive copolymer may be added to the thick stock or thin stock, preferably the thin stock. The copolymer may be added at one feed point, or may be split fed such that the copolymer is fed simultaneously to two or more separate feed points. Typical stock addition points

include feed point(s) before the fan pump, after the fan pump and before the pressure screen, or after the pressure screen.

[0083] The copolymers useful in the invention are employed in a proportion of from about 0.005 kg to about 5 kg of active polymer per metric ton of cellulosic pulp, based on the dry weight of the pulp. The concentration of copolymer is preferably from about 0.025 kg to about 2.5 kg of active polymer per metric ton of dried cellulosic pulp. The concentration of copolymer is more preferably from about 0.1 kg to about 1 kg of active polymer per metric ton of dried cellulosic pulp.

[0084] The present invention will now be further described with reference to a number of specific examples that are to be regarded solely as illustrative and not restricting the scope of the present invention.

EXAMPLES

[0085] The following materials are used in the preparation of the examples provided.

[0086] Atlas® G-946 is sorbitan monooleate marketed by Uniqema, New Castle, DE.

[0087] Hypermer® B246SF is triblock polymeric surfactant marketed by Uniqema, New Castle, DE.

[0088] OA is t-octylacrylamide obtained from Monomer-Polymer & Dajac Labs, Inc., Feasterville, PA.

[0089] COPS1 is Sipomer® COPS1, a sodium alkylhydroxypropyl sulfonate monomer marketed by Rhodia, Inc., Cranbury, NJ.

[0090] BEM-25 is Sipomer® BEM-25, a behenyl polyethoxymethacrylate monomer marketed by Rhodia, Inc., Cranbury, NJ.

[0091] SEM-25 is Sipomer® SEM-25, a tristyrylphenol polyethoxymethacrylate monomer marketed by Rhodia, Inc., Cranbury, NJ.

[0092] 5010 is Maxemul® 5010, an alkenyl functional non-ionic surfactant marketed by Uniqema, New Castle, DE.

[0093] Acrylic acid was obtained from Rohm and Haas, Philadelphia, PA.

[0094] Acrylamide was obtained from Cytec, Inc., Mobile, AL

Example 1

[0095] To a suitable reaction flask equipped with an overhead mechanical stirrer, thermometer, nitrogen sparge tube, and condenser, charge an oil phase of paraffin oil (135.0g, Escaid® 110 oil, Exxon – Houston, TX) containing surfactants (4.5g Atlas® G-946 and 9.0g Hypermer® B246SF), to which 1.77g of OA (t-octylacrylamide) is added. The temperature of the oil phase is adjusted to 37°C.

[0096] An aqueous phase is prepared separately which comprises 53-wt. % acrylamide solution in water (126.5g), acrylic acid (68.7g), deionized water (62.12g), and Versenex® 80 (Dow Chemical) chelant solution (0.7g). The aqueous phase is then adjusted to pH 5.4 with the addition of ammonium hydroxide solution in water (33.1g, 29.4-wt. % as NH₃). The temperature of the aqueous phase after neutralization is 39°C.

[0097] The aqueous phase is then charged to the oil phase while simultaneously mixing with a homogenizer to obtain a stable water-in-oil emulsion. This emulsion is then mixed with a 4-blade glass stirrer while being sparged with nitrogen for 60 minutes. During the nitrogen sparge the temperature of the emulsion is adjusted to 50±1°C. Afterwards, the sparge is discontinued and a nitrogen blanket implemented.

[0098] The polymerization is initiated by a 3 wt% solution of lauroyl peroxide (LP) in toluene at a level of 20 molar ppm LP on a total monomer molar basis to start the polymerization, 10 molar ppm LP on a total monomer molar basis after one hour.

of polymerization, and 10 molar ppm LP on a total monomer molar basis after four hours of polymerization.

[0099] The batch is then cooled to room temperature and the product collected.

[0100] The molar ratio of acrylic acid to acrylamide to OA is 50: 49.25: 0.75.

Example 2 - 5

[0101] Examples 2-5 were prepared as described in example 1 except that the molar composition of monomer was as shown in Table 1.

Example	Monomer 1		Monomer 2		Monomer 3	
	Monomer^(a)	%^(b)	Monomer^(a)	%^(b)	Monomer^(a)	%^(b)
2	Acrylic Acid	50.00	Acrylamide	49.75	COPS1	0.25
3	Acrylic Acid	50.00	Acrylamide	49.60	BEM-25	0.40
4	Acrylic Acid	50.00	Acrylamide	49.90	SEM-25	0.10
5	Acrylic Acid	50.00	Acrylamide	49.70	5010	0.30

(a) Monomer(s) used in the example.

(b) Mole % of monomer, based on total monomer

[0102] Prior to inverting the emulsions of Examples 1 to 5 for analysis or use, ~2 wt. % of a breaker surfactant, for example a 80:20 by weight mixture of Tergitol 15-S-9 (Dow, Midland, MI) and Aerosol-OT-S (Cytec Industries, West Patterson, NJ), was added. The pH of the inverted water-soluble anionic copolymers was then adjusted to a minimum of 7.0 with aqueous sodium hydroxide or ammonium hydroxide, as required.

Examples 6-10

[0103] Example 6 is PerForm® 9232 Retention and Drainage Aid (Hercules Incorporated, Wilmington, DE)

[0104] Example 7 is Acrysol® TT-935 a HASE material marketed by Rohm and Haas Company, Philadelphia, PA.

[0105] Example 8 is a copolymer of butylacrylate and acrylic acid, monomer molar ratio at 50:50, obtained from Polysciences, Inc., Warrington, PA.

[0106] Example 9 is poly(*N*-isopropylacrylamide) obtained from Scientific Polymer Products, Inc., Ontario, NY.

[0107] Example 10 is poly(*N,N*-dimethylacrylamide) obtained from Scientific Polymer Products, Inc., Ontario, NY.

PERFORMANCE TESTS

[0108] The technique of paper sheet formation and retention/drainage is well known in the art; for example, see *Handbook for Pulp and Paper Technologist*, G.A. Snook, ed., (TAPPI Press, Atlanta, GA, 1989) and *PULP AND PAPER, Chemistry and Chemical Technology*, 3rd edition, J. P. Casey, ed., (Wiley-Interscience, New York, 1981).

[0109] To evaluate the performance of the water-soluble hydrophobic polymers and copolymers examples of the present invention, a series of retention tests and/or drainage tests were conducted. PerForm® SP9232 retention and drainage aid, a product of Hercules Incorporated, was used as a comparative example (Example 6) for examples 1 to 5. Unless otherwise stated, all percentages, parts, etc., are by weight.

[0110] The furnish employed in this series of tests is a synthetic alkaline furnish. This furnish is prepared from about 70% by wt of hardwood and 30% by wt of softwood dried market lap pulps, and from water and further materials. First the hardwood and softwood dried market lap pulp are separately refined in a laboratory

Valley Beater (Voith, Appleton, WI). These pulps are then added to an aqueous medium.

[0111] The aqueous medium utilized in preparing the furnish comprises a mixture of local hard water and deionized water to a representative hardness. Inorganic salts are added in amounts so as to provide this medium with a total alkalinity of 75 ppm as CaCO₃ and hardness of 100 ppm as CaCO₃.

[0112] To prepare the furnish, the hardwood and softwood are dispersed into the aqueous medium at typical weight ratios of hardwood and softwood (typically about 70:30). Precipitated calcium carbonate (PCC) is introduced into the furnish at 25 weight percent, based on the combined dry weight of the pulps, so as to provide a final furnish comprising 80 % fiber and 20 % PCC filler.

[0113] To the pulp slurry, a cationic potato starch, Stalok® 400 (A.E. Staley, Decatur, IL), is added at a level of 5 kg per metric ton, based on dry pulp, and then alum, (aluminum sulfate octadecahydrate available as a 50% solution from Delta Chemical Corporation, Baltimore, MD), is added at a level of 2.5 kg per metric ton. Next, a cationic flocculant, (Perform® PC 8138, Hercules Incorporated) is added at a level of 0.25 kg/metric ton, based on dry pulp.

[0114] For examples 1 to 5, copolymers were then added at a level of 0.4 kg of active component / metric ton of furnish solids. The vacuum drainage time of the water compatible hydrophobic copolymers and the comparative copolymer (example 6) were measured. The control is the pulp composition described above but without the water compatible hydrophobic copolymers.

[0115] The following is a description of the test procedures.

[0116] The Britt jar retention test (Paper Research Materials, Inc., Gig Harbor, WA) is known in the art. In the Britt jar retention test a specific volume of furnish is mixed under dynamic conditions and an aliquot of the furnish is drained through the bottom screen of the jar, so that the level of fine materials which are retained can be

quantified. The Britt jar utilized for the present tests is equipped with 3 vanes on the cylinder walls to induce turbulent mix, and a 76 μm screen in the bottom plate.

[0117] A series of drainage tests were also conducted utilizing a vacuum drainage test (VDT) developed to differentiate the activity between the microparticle technology and conventional linear flocculants. The results of this testing demonstrate the ability of the VDT to differentiate drainage aids in both CPAM and APAM programs by the magnitude of the drainage time.

[0118] The device setup is similar to the Buchner funnel test as described in various filtration reference books, for example see *Perry's Chemical Engineers' Handbook*, 7th edition, (McGraw-Hill, New York, 1999) pp.18-78. The VDT consists of a 300-ml magnetic Gelman filter funnel, a 250-ml graduated cylinder, a quick disconnect, a water trap, and a vacuum pump with a vacuum gauge and regulator. The VDT test is conducted by first setting the vacuum to the desired level, typically 10 inches Hg, and placing the funnel properly on the cylinder. Next, 250g of 0.5 wt. % paper stock is charged into a beaker and then the required additives according to treatment program (e.g., starch, alum, and testing flocculants) are added to the stock under the agitation provided by an overhead mixer. The stock is then poured into the filter funnel and the vacuum pump is turned on while simultaneously starting a stopwatch. The drainage efficacy is reported as the time required to obtain 230 ml of filtrate.

[0119] The principle of the VDT is based on the cake filtration theory, for reference see L. Svarovsky, editor, *Solid-Liquid Separation*, 3rd edition (London, Butterworths, 1990), Chapter 9. Initially, the solids in the slurry are deposited on a relative thin filter medium that serves to support the filter cake. The successive deposits of solids layer to form the filter cake, or mat. The rate of filtrate passing through the filter cake (or mat) is dependent on floc density, floc size distribution in the mat, and levels of residual polymeric materials in the aqueous phase. A flocculant that forms dense and uniform-sized flocs and has low residual level in water (i.e., good formation characteristics) will demonstrate good drainage in the VDT test, and vice versa.

[0120] The data set forth in Table 2 illustrates the retention and drainage activity of the water-compatible hydrophobic copolymers.

TABLE 2
PERFORMANCE DATA

Example	Retention ^(a) (%)	Drainage ^(b) (sec.)
Control	40.7	34.0
1	95.7	13.4
2	94.4	16.8
3	92.2	16.4
4	93.7	13.4
5	96.1	15.3
6	93.4	15.3

(a) First pass fine retention as measured by Britt Jar test

(b) Drainage as measured by the vacuum drainage test

[0121] The data in Table 2 demonstrate that the water-soluble hydrophobic polymers and copolymers of the present invention provide a significant improvement over the control material.

[0122] The drainage test data for examples 7 to 10 are shown in Table 3. Note that the use levels of these copolymers was 0.25 kg of active polymer per metric ton of furnish solids.

TABLE 3
PERFORMANCE DATA

Example	Amount Added (kg/MT)	Drainage ^(a) (Sec)
Control	-	40.0
7	0.25	36.8
8	0.25	38.4

9	0.25	39.9
10	0.25	37.6

(a) Drainage is measure by the vacuum drainage test

[0123] These data indicate that these materials provide an improvement in drainage compared to the control.

[0124] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to an exemplary embodiment, it is understood that the words that have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein. For example, cationic and/or amphoteric copolymers prepared per the preferred polymerization conditions may also exhibit activity in papermaking applications. The water-soluble anionic copolymers of the present invention may also exhibit activity in other applications such as coagulants and/or flocculants in wastewater treatment applications, or as rheology modifiers in paints, coatings, drilling fluids and/or cement processing applications.

CLAIMS

1. A method of improving retention and drainage in a papermaking process wherein the improvement comprising adding to a papermaking slurry, a water compatible hydrophobic polymer.
2. The method of claim 1 wherein the water compatible hydrophobic polymer is a synthetic copolymer that contains at least one hydrophobic monomer.
3. The method of claim 2 wherein the synthetic copolymer is formed from at least one monomer comprising at least one hydrophobic monomer selected from lauryl acrylate and octylacrylamide.
4. The method of claim 2 wherein the synthetic copolymer is formed from at least one monomer comprising at least one non-ionic monomer selected from acrylamide, methacrylamide, *N,N*-dialkylacrylamides, *N*-alkylacrylamides, *N*-vinyl methacetamide, *N*-vinyl methylformamide, and *N*-vinyl pyrrolidone.
5. The method of claim 4 wherein the synthetic copolymer is formed from monomers further comprising at least one anionic monomer selected from the free acid or salt of: acrylic acid; methacrylic acid, maleic acid; itaconic acid; acrylamidoglycolic acid; 2-acrylamido-2-methyl-1-propanesulfonic acid; 3-allyloxy-2-hydroxy-1-propanesulfonic acid; styrenesulfonic acid; vinylsulfonic acid; vinylphosphonic acid; and 2-acrylamido-2-methylpropane phosphonic acid.
6. The method of claim 4 wherein the synthetic copolymer is from monomers further comprising at least one cationic monomer selected from the free base or salt of: diallyldimethylammonium halide; dialkylaminoalkyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethyl aminopropyl (meth)acrylate, 2-hydroxydimethyl aminopropyl (meth)acrylate, aminoethyl (meth)acrylate, *N,N*-dimethylaminoethylacrylamide, and acryloyloxyethyl trimethyl ammonium chloride.

7. The method of claim 5 wherein at least one anionic monomer is selected from the free acid or salt of: acrylic acid, styrenesulfonic acid, or 2-acrylamido-2-methyl-1-propanesulfonic acid.
8. The method of claim 1 further comprising adding a siliceous material to the paper making slurry.
9. The method of claim 8 wherein the siliceous material is selected from the group consisting of silica based particles, silica microgels, amorphous silica, colloidal silica, anionic colloidal silica, silica sols, silica gels, polysilicates, polysilicic acid, and combinations thereof.
10. The method of claim 2 wherein the water compatible hydrophobic copolymer comprises anionic monomers.
11. The method of claim 4 wherein the non-ionic monomer comprises acrylamide.
12. The method of claim 2 wherein the water compatible hydrophobic polymer comprises cationic monomers.
13. A composition comprising a water compatible hydrophobic polymer and cellulosic fiber.
14. The method of claim 1 wherein the water compatible hydrophobic polymer is selected from the group consisting of a hydrophobic alkali swellable emulsion, an ethoxylated urethane polymer, a fluorinated polymer, a hydrophobically modified natural polymer or mixtures thereof.
15. The method of claim 2 wherein the hydrophobic monomer is present in the polymer in an amount of less than about 5% on a molar basis.
16. The method of claim 2 wherein the hydrophobic monomer is present in the polymer in an amount of less than about 2% on a molar basis.

17. The method of claim 1 wherein the water compatible hydrophobic polymer is added to the papermaking slurry in an amount of from about 0.005 kg to about 5 kg of active polymer per metric ton of cellulosic pulp.

18. The method of claim 1 wherein the water compatible hydrophobic polymer is added to the papermaking slurry in an amount of from about 0.025 kg to about 2.5 kg of active polymer per metric ton of cellulosic pulp.

19. A method of improving retention and drainage in a papermaking process wherein the improvement comprising adding to a papermaking slurry, a water compatible hydrophobic polymer, wherein the water compatible hydrophobic polymer comprises acrylamide, acrylic acid and octylacrylamide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/046946

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H21/10

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	<p>WO 01/40578 A (HERCULES INCORPORATED) 7 June 2001 (2001-06-07) page 1, line 2 - line 6 page 1, line 22 - line 23 page 4, line 4 - page 8, line 39 page 12, line 11 - line 14 page 28, line 1 - page 29, line 9 claims 1-20</p>	<p>1-7,10, 11,13-20</p>
X	<p>US 6 417 268 B1 (ZHANG HUASHI T ET AL) 9 July 2002 (2002-07-09) column 7, line 22 - column 9, line 45 claims 1,9</p>	<p>1-7,10, 11,13-20</p>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document but published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
O document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 26 April 2006	Date of mailing of the international search report 08/05/2006
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2005/046946

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	<p>US 2004/143039 A1 (HOLLOMON MARTHA ET AL) 22 July 2004 (2004-07-22)</p> <p>page 1, paragraph 2 page 1, paragraph 11 page 2, paragraph 14 - paragraph 18 page 2, paragraph 20 - paragraph 22 page 3, paragraph 25 - paragraph 26 page 4, paragraph 36 page 4, paragraph 41 page 4, paragraph 44 page 4, paragraph 46 page 5, paragraph 49</p> <p>-----</p>	1,2, 4-11,13, 14,18,19
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Information on patent family members

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