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(54) **METHOD FOR USING HYDROPHOBICALLY ASSOCIATIVE POLYMERS IN PREPARING CELLULOSIC FIBER COMPOSITIONS, AND CELLULOSIC FIBER COMPOSITIONS INCORPORATING THE HYDROPHOBICALLY ASSOCIATIVE POLYMERS**

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(57) **ABSTRACT**

A papermaking method and a composition which utilize, as a drainage aid, a water soluble hydrophobically associative polymer which is a copolymer prepared from monomers which include a hydrophobic ethylenically unsaturated monomer, and one or more of a nonionic ethylenically unsaturated monomer, a cationic ethylenically unsaturated monomer, and an anionic ethylenically unsaturated monomer.

**METHOD FOR USING HYDROPHOBICALLY
ASSOCIATIVE POLYMERS IN PREPARING
CELLULOSIC FIBER COMPOSITIONS, AND
CELLULOSIC FIBER COMPOSITIONS
INCORPORATING THE HYDROPHOBICALLY
ASSOCIATIVE POLYMERS**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

[0001] This application is a continuation in part of application Ser. No. 09/455,027.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to using hydrophobically modified water-soluble polymers, also referred to hereinafter as hydrophobically associative polymers or HAPs, in the preparation of cellulosic fiber compositions. The present invention further relates to cellulosic fiber compositions, such as paper and paperboard, which incorporate the HAPs

[0004] 2. Description of Background and Other Information

[0005] The making of cellulosic fiber sheets—particularly paper and paperboard—includes the following:

[0006] producing an aqueous slurry of cellulosic fiber, which may also contain inorganic mineral extenders or pigments;

[0007] depositing this slurry on a moving papermaking wire or fabric; and

[0008] forming a sheet from the solid components of the slurry by draining the water.

[0009] 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 or more rapid, or to attain specific properties in the final paper product.

[0010] 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 drainage and/or retention aids.

[0011] 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 method speeds. Improved dewatering can also result in a dryer sheet in the press and dryer sections, resulting in reduced steam consumption. Yet further, this is the stage in the papermaking method that determines many sheet final properties.

[0012] 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 method effluent or accumulate to high levels in the recirculating white water loop, potentially causing deposit buildup and

impairing paper machine drainage. Additionally, insufficient retention of the fine solids increases the papermakers' cost due to loss of additives intended to be adsorbed on the fiber to provide the respective paper opacity, strength, or sizing property.

[0013] High MW water-soluble polymers with either cationic or anionic charge have traditionally been used as retention and drainage aids. Recent development of inorganic microparticles, known as retention and drainage aids, 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. Pat. Nos. 4,294,885 and 4,388,150 teach the use of starch polymers with colloidal silica. U.S. Pat. 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. Pat. Nos. 5,274,055 and 5,167,766 disclose using chemically crosslinked organic microparticle or micropolymers as retention and drainage aids in papermaking process.

[0014] Hydrophobically modified water-soluble polymers, also referred to hereinafter as hydrophobically associative polymers or HAPs, are known to those skilled in the art, for example see the *Encyclopedia of Polymer Science and Engineering*, 2nd edition, 17, 772-779. U.S. Pat. Nos. 4,432,881 and 4,861,499 disclose the use of these polymers as thickening agents for paint formulations and for applications in oil recovery methods, such as drilling mud formulations, fracturing fluids, liquid mobility control agents, friction reducing agents, hydraulic fluids, and lubricants. These patents do not teach or suggest the use of the polymers in cellulosic compositions such as paper, or in methods for preparing these cellulosic compositions.

[0015] U.S. Pat. No. 4,305,860 discloses the preparation of stable, pumpable, solvent-free polyampholyte lattices (colloidal dispersions of a solid copolymer in water) characterized by their colloidal nature and their high solids content and low bulk viscosity. The lattices are prepared by polymerizing about 10 to 30 mole % of at least one cationic monomer, 5 to 30 mole % of at least one anionic monomer, 15 to 35 mole % of at least one hydrophobic monomer and 5 to 70 mole % of at least one non-ionic hydrophilic monomer, with the monomer percentages totaling 100 mole %, in the presence of water and a free-radical initiator and optionally a chelating agent. The lattices are taught to be particularly useful as pigment retention and drainage aids in the manufacture of paper and may be added to the pulp while the latter is in the headbox, beater, hydropulper or stock chest. The high hydrophobic group content (>15 mole %) makes this disclosed polymer insoluble in aqueous solution, which distinguishes itself from the water-soluble HAP polymers disclosed in the present invention.

[0016] EP 0 896 966 A1 discloses the preparation of associative polymers by inverse emulsion procedures utilizing a pendant acrylate hydrophobe chain extended with a polyoxyethylene group. The associative acrylic polymers comprise from 95 to 99.95% moles of at least one monomer selected from neutral ethylene, anionic or cationic monomers, from 0.05 to 5% moles of at least one acrylic monomer containing the radical 2,4,6-triphenoethyl benzene, and from 0 to 0.2% moles of at least one polyunsaturated monomer. It is preferred that the associative polymers contain from 0.5 to

5 molar % of polyoxyethylene 2,4,6-triphenoethyl benzene methacrylate. The polymers may be used in diverse areas, such as paints, glues and adhesives, construction, textiles and paper. The composition is claimed for use as a thickener, flocculation agent, and/or charge retention agent; no data or further specification is provided for the utilization.

SUMMARY OF THE INVENTION

[0017] The present invention is directed to a cellulosic fiber composition, particularly a cellulosic sheet such as paper or paperboard. The invention is also directed to a method for making the composition.

[0018] The present invention relates to a method of making a cellulosic fiber composition that includes adding, to a cellulosic pulp slurry, a HAP and relates to a cellulosic fiber composition including an aqueous slurry of cellulosic pulp and a HAP. The HAP is preferably a copolymer including hydrophobic groups that are capable of forming a physical network structure through hydrophobic association, and has at least one monomer selected from the group consisting of nonionic ethylenically unsaturated monomers, cationic ethylenically unsaturated monomers, or anionic ethylenically unsaturated monomers.

[0019] The HAP is highly associative and forms a network structure in aqueous solution as demonstrated by a $\tan \delta$ value less than an analogous polymer without the hydrophobic modification, as determined by viscoelastic characterizations of a 0.5% solution. A significant improvement in retention and drainage activity is obtained when HAP is applied to a pulp furnish, and at the same time a satisfactory sheet formation is maintained, which is the unique property that a traditional flocculant could not achieve. The HAP is usually water soluble.

[0020] The HAP may include at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent, and at least one monomer selected from a nonionic ethylenically unsaturated monomer, a cationic ethylenically unsaturated monomer, or an anionic ethylenically unsaturated monomer with the proviso that the at least one hydrophobic ethylenically unsaturated monomer does not contain 2,4,6-triphenoethyl benzene.

[0021] The at least one hydrophobic ethylenically unsaturated monomer may be an ethylenically unsaturated monomer having at least one pendant hydrophobic group of the general structure:

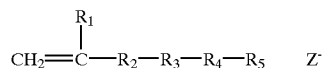


FIG. 1

[0022] wherein R_1 is hydrogen or methyl; R_2 , when present, is $\text{---CH}_2\text{---}$, ---C(O)---O--- , ---O---C(O)--- , $\text{---C(O)---NR}_6\text{---}$, $\text{---NR}_6\text{---C(O)---}$, or ---O--- ; R_3 , when present, is $\text{---(---CH}_2\text{---CHR}_1\text{---O---)}_n\text{---}$, $\text{C}_1\text{---C}_{20}$ alkyl, or $\text{C}_1\text{---C}_{20}$ hydroxy alkyl wherein n equals 1 to 40 and R_1 is as described above; R_4 , when present, is $\text{---NR}_6\text{---}$ or $\text{---N}^+(\text{R}_6)_2\text{---}$; R_5 is the pendant hydrophobic group selected from one or more of $\text{C}_4\text{---C}_{20}$ alkyls, $\text{C}_4\text{---C}_{20}$ cycloalkyls,

polynuclear aromatic hydrocarbon groups, alkaryls wherein alkyl has one or more carbons, or haloalkyls of four or more carbons; R_6 , when present, is hydrogen, methyl, $\text{CH}_2=\text{CR}_1\text{---CH}_2\text{---}$, equivalent to the pendent hydrophobic group R_5 as described above, or a mixture thereof; and Z , present when R_4 is $\text{---N}^+(\text{R}_6)_2\text{---}$, is the conjugated base of an acid; with the proviso that R_5 is not 2,4,6-triphenoethyl benzene.

[0023] The polynuclear aromatic hydrocarbon group may be naphthyl. The haloalkyls of four or more carbons may be perfluoroalkyls which preferably are selected from one or more of $\text{C}_4\text{F}_9\text{---C}_{20}\text{F}_{41}$. The pendant hydrophobic group may be polyalkyleneoxy groups wherein the alkylene is propylene or higher alkylene and there is at least one alkyleneoxy unit per hydrophobic moiety or may be selected from one or more of $\text{C}_4\text{---C}_{20}$ alkyl groups or preferably from one or more of $\text{C}_8\text{---C}_{20}$ alkyl groups.

[0024] Preferably the hydrophobic ethylenically unsaturated monomer depicted in FIG. 1 may be selected from one or more hydrocarbon esters of ethylenically unsaturated carboxylic acids and their salts, N-alkyl ethylenically unsaturated amides, α -olefins, vinyl esters, vinyl ethers, N-vinyl amides, alkylstyrenes, alkyl polyethyleneglycol (meth)acrylates, or N-alkyl ethylenically unsaturated cationic monomers. The ethylenically unsaturated carboxylic acids may preferably be selected from the $\text{C}_{10}\text{---C}_{20}$ alkyl esters of acrylic and methacrylic acid and more preferably from dodecyl acrylate or dodecyl methacrylate. The ethylenically unsaturated amides may preferably be selected from N-octadecyl acrylamide, N-octadecyl methacrylamide, or N,N-dioctyl acrylamide. The α -olefins may preferably be selected from 1-octene, 1-decene, 1-dodecene, or 1-hexadecene. The vinyl esters may preferably be vinyl laurate or vinyl stearate. The vinyl alkyl ethers may preferably be dodecyl vinyl ether or hexadecyl vinyl ether. The N-vinyl amides may preferably be N-vinyl lauramide or N-vinyl stearamide. The alkylstyrene may preferably be t-butyl styrene. The alkyl polyethyleneglycol (meth)acrylates may preferably be selected from laurylpolyethoxy(23) methacrylate. The N-alkyl ethylenically unsaturated cationic monomers may preferably be selected from the $\text{C}_{10}\text{---C}_{20}$ alkyl halide quaternary salts of methyldiallylamine, N,N-dimethylaminoalkyl(meth)acrylates, and N,N-dialkylaminoalkyl(meth)acrylamides.

[0025] The at least one nonionic ethylenically unsaturated monomer may be one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone. The N-alkylacrylamide is preferably N-methylacrylamide and the N,N-dialkylacrylamide is preferably N,N-dimethylacrylamide. The at least one nonionic ethylenically unsaturated monomer is preferably one or more of acrylamide, methacrylamide, or N-methylacrylamide and more preferably acrylamide.

[0026] The at least one anionic ethylenically unsaturated monomer may be one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof, preferably one or more of acrylic acid, methacrylic acid or the salts thereof and more preferably one or more of the sodium or ammonium salts of acrylic acid.

[0027] The at least one cationic ethylenically unsaturated monomer may be selected from one or more of diallylamine, the (meth)acrylates of dialkylaminoalkyl compounds, the (meth)acrylamides of dialkylaminoalkyl compounds, the N-vinylamine hydrolyzate of N-vinylformamide, and the salts and quaternaries thereof. The quaternary salt of diallylamine may preferably be diallyldimethylammonium chloride. The dialkylaminoalkyl (meth)acrylamide may preferably be N,N-dimethylaminopropylacrylamide, the acid or quaternary salt thereof may preferably be N,N,N-trimethylaminopropylacrylamide chloride. The dialkylaminoalkyl (meth)acrylate may preferably be N,N-dimethylaminoethylacrylate, the acid or quaternary salt thereof may preferably be N,N,N-trimethylaminoethylacrylate chloride. The at least one cationic ethylenically unsaturated monomer may also be selected from one or more of the compounds of the following general formulae:

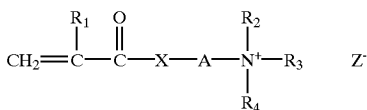


FIG. 2

[0028] wherein

[0029] R_1 is hydrogen or methyl,

[0030] R_2 , R_3 , and R_4 are hydrogen, alkyl of C_1 to C_3 , or hydroxyethyl,

[0031] R_2 and R_3 or R_2 and R_4 can combined to form a cyclic ring containing one of more hetero atoms,

[0032] Z is the conjugate base of an acid,

[0033] X is oxygen or NR_1 wherein R_1 is as defined above, and

[0034] A is an alkylene group of C_1 to C_{12} ; or

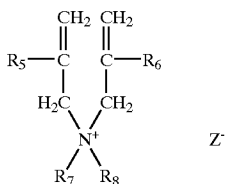


FIG. 3

[0035] wherein

[0036] R_5 and R_6 are hydrogen or methyl,

[0037] R_7 and R_8 are hydrogen, alkyl of C_1 to C_3 , or hydroxyethyl; and

[0038] Z is as defined above;

[0039] or N-vinylformamides and the associated hydrolyzates as represented by recurring units of

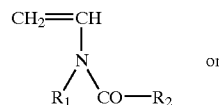


FIG. 4

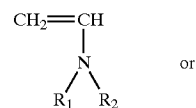


FIG. 5

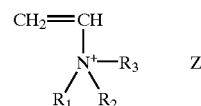


FIG. 6

[0040] wherein

[0041] R_1 , R_2 and R_3 are each H or C_1 to C_3 alkyl, and

[0042] Z is defined as above.

[0043] It is noted that the description of the hydrophobic ethylenically unsaturated monomer encompasses the cationic ethylenically unsaturated monomers depicted in FIGS. 2-6 wherein, for example, the definition of R_2 of FIGS. 2, 4-5 and R_7 of FIG. 3 are substituted with pendant hydrophobic moiety R_5 of FIG. 1.

[0044] It is preferable that HAP in accordance with this invention (an 0.5% aqueous solution of the HAP) have a dynamic oscillation frequency sweep tan delta value at 0.0068 Hz less than an analogous polymer absent the hydrophobic ethylenically unsaturated monomer, most preferably less than 1. It is also preferable that the at least one hydrophobic ethylenically unsaturated monomer groups be present in an amount from about 0.01 mole percent to about 10 mole percent, and more preferably in an amount from about 0.1 mole percent to about 5.0 mole percent.

[0045] The HAP used in this invention may be an anionic, nonionic, cationic or amphoteric copolymer, and preferably an anionic copolymer. The anionic copolymer may include at least one hydrophobic ethylenically unsaturated monomer and at least one anionic ethylenically unsaturated monomer and may further include at least one nonionic ethylenically unsaturated monomer.

[0046] The anionic copolymer may include about 0.001 mole percent to about 10 mole percent of the at least one hydrophobic ethylenically unsaturated monomer, about 1 mole percent to about 99.999 mole percent of the at least one anionic ethylenically unsaturated monomer, and about 1 mole percent to about 99.999 mole percent of the at least one nonionic ethylenically unsaturated monomer; preferably about 0.01 mole percent to about 5 mole percent of the at least one hydrophobic ethylenically unsaturated monomer, about 10 mole percent to about 90 mole percent of the at least one anionic ethylenically unsaturated monomer, and about 10 mole percent to about 90 mole percent of the at least one nonionic ethylenically unsaturated monomer; and more preferably about 0.1 mole percent to about 2.0 mole percent of the at least one hydrophobic ethylenically unsaturated monomer, about 10 mole percent to about 90 mole percent of the at least one anionic ethylenically unsaturated monomer, and about 10 mole percent to about 90 mole percent of the at least one nonionic ethylenically unsaturated monomer.

urated monomer, about 30 mole percent to about 70 mole percent of the at least one anionic ethylenically unsaturated monomer, and about 50 mole percent to about 70 mole percent of the at least one nonionic ethylenically unsaturated monomer.

[0047] The inventive cellulosic pulp slurry containing the HAP may also include, at the option of the skilled worker, other components such as at least one flocculant, at least one starch, at least one inorganic or organic coagulant, or at least one filler.

[0048] The present invention also includes a cellulosic sheet produced by the inventive method. The cellulosic sheet may include paper and paperboard incorporating the HAP.

[0049] The present invention also relates to a method of making a cellulosic fiber composition which includes adding, to a cellulosic pulp slurry, a HAP and relates to a cellulosic fiber composition including an aqueous slurry of cellulosic pulp and a HAP, where the HAP includes at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent and selected from one or more of C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid; and at least one monomer selected from: a) about 1 mole percent to about 99.999 mole percent of at least one nonionic ethylenically unsaturated monomer selected from one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone; b) about 1 mole percent to about 99.999 mole percent of at least one anionic ethylenically unsaturated monomer selected from one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl-(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof; or c) about 1 mole percent to about 99.999 mole percent of at least one cationic ethylenically unsaturated monomer selected from one or more of diallylamine, the (meth)acrylates of dialkylaminoalkyl compounds, the (meth)acrylamides of dialkylaminoalkyl compounds, the N-vinylamine hydrolyzate of N-vinylformamide, and the salts and quaternaries thereof.

[0050] The HAP may preferably include at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent and selected from one or more of C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid; and at least one monomer selected from: a) about 1 mole percent to about 99.999 mole percent of at least one nonionic ethylenically unsaturated monomer selected from one or more of acrylamide, methacrylamide, or N-alkylacrylamides; b) about 1 mole percent to about 99.999 mole percent of at least one anionic ethylenically unsaturated monomer selected from one or more of acrylic acid, methacrylic acid or the salts thereof; or c) about 1 mole percent to about 99.999 mole percent of at least one cationic ethylenically unsaturated monomer selected from one or more of N,N-dialkylaminoalkyl acrylates, N,N-dialkylaminoalkyl methacrylates, the acid or quaternary salts thereof. Preferably, the at least one hydrophobic ethylenically unsaturated monomer may be selected from one or more of dodecyl acrylate or dodecyl

methacrylate, the nonionic ethylenically unsaturated monomer may be acrylamide, the at least one anionic ethylenically unsaturated monomer may be selected from one or more of the sodium or ammonium salts of acrylic acid, and the cationic ethylenically unsaturated monomer may be the methyl chloride quaternary of N,N-dimethylaminoethylacrylate.

[0051] To the aforementioned pulp slurry containing the HAP may be added, at the option of the skilled worker, additional components, such as at least one flocculant, at least one starch, at least one coagulant, or at least one filler.

[0052] The present invention also relates to a method of making a cellulosic fiber composition which includes adding, to a cellulosic pulp slurry, an anionic HAP and relates to a cellulosic fiber composition including an aqueous slurry of cellulosic pulp and an anionic HAP, where the anionic HAP preferably includes at least one hydrophobic ethylenically unsaturated monomer selected from one or more of lauryl acrylate or lauryl methacrylate, the at least one nonionic ethylenically unsaturated monomer being acrylamide, and the at least one anionic ethylenically unsaturated monomer being acrylic acid. To the aforementioned pulp slurry containing the HAP may be added, at the option of the skilled worker, additional components, such as at least one flocculant, at least one starch, at least one inorganic or organic coagulant, or at least one filler. The invention also relates to a cellulosic sheet produced by the aforesaid method and from the aforesaid composition. The cellulosic sheet may include paper and paperboard incorporating the HAP.

[0053] The cellulosic fiber composition of the invention preferably comprises the HAP and its viscoelasticity properties, as discussed. Preferred cellulosic fiber compositions of the invention include paper.

DESCRIPTION OF THE INVENTION

[0054] 1. Definitions

[0055] As used herein, the term "HAP" refers to the hydrophobically associative polymer of this invention.

[0056] As used herein, the term "hydrocarbon" includes "aliphatic", "cycloaliphatic", and "aromatic". The terms "aliphatic" and "cycloaliphatic"—unless stated otherwise—are understood as including "alkyl", "alkenyl", "alkynyl", and "cycloalkyl". The term "aromatic"—also unless stated otherwise—is understood as including "aryl", "aralkyl", and "alkaryl".

[0057] Hydrocarbon groups are understood as including both nonsubstituted hydrocarbon groups and substituted hydrocarbon groups, with the latter referring to the hydrocarbon portion bearing additional substituents besides the carbon and hydrogen. Correspondingly, aliphatic, cycloaliphatic, and aromatic groups are understood as including both nonsubstituted aliphatic, cycloaliphatic, and aromatic groups and substituted aliphatic, cycloaliphatic, and aromatic groups, with the latter referring to the aliphatic, cycloaliphatic, and aromatic portion bearing additional substituents besides the carbon and hydrogen.

[0058] Also as discussed herein, copolymers are understood as including polymers consisting of, or consisting substantially of or consisting essentially of, two different

monomeric units. Copolymers are further understood as including polymers incorporating three or more different monomeric units, e.g., terpolymers, etc.

[0059] 2. Method of the Invention

[0060] The invention comprises a method of making cellulosic fiber compositions—particularly cellulosic fiber webs, more particularly cellulosic fiber sheets, and still more particularly paper and paperboard. This method comprises the addition of at least one HAP to a suitable paper furnish—e.g., a cellulosic fiber pulp or stock, particularly a cellulosic wood fiber pulp or stock.

[0061] Preferably this polymer is added to a slurry comprising an aqueous suspension of the furnish. Also as a matter of preference, a cellulosic web—particularly a sheet, and still more particularly paper or paperboard—is formed from the slurry.

[0062] The method of the invention can entail the steps of providing a paper furnish comprised of cellulosic fibers with or without additional mineral fillers suspended in water, depositing the furnish on a papermaking wire or fabric, and forming a sheet out of the solid components by dewatering the slurry, with the at least one HAP being added at one or more points during this method. Preferably, this polymer is introduced into the fibrous slurry prior to the dewatering sequence.

[0063] The HAP serves to provide an increase in retention of fine particles and/or an increase in fibrous dewatering. This polymer is particularly effective in providing for retention both of filler—where it is employed—and of cellulosic fiber fines, these fines being generated from the fiber during the method of the invention. It is postulated that HAPs form physical network structure through the hydrophobic group in aqueous solution as demonstrated by their viscoelasticity behavior. Since the three-dimension structure of the HAP is less absorbed on the particle surface, better bridging is provided between particles, which leads to better retention and drainage activity.

[0064] Viscoelastic behavior as discussed herein (Rheology: Principles, Measurements, and Applications, C. W. Macosko, Wiley, New York, N.Y.) denotes a time dependent response to a deformation, i.e., at short times the material is hard and glassy, whereas at longer times the material is rubbery or viscous. A common way to measure this phenomenon is by stress relaxation, where an instantaneous strain is imposed upon a material, and the resultant stress decay over time is recorded. A purely viscous material would exhibit a stress of zero once the strain becomes constant, while an elastic solid would show no stress decay. A viscoelastic material would exhibit a stress decay between these two extremes; thus exhibiting combined elastic and viscous response, or viscoelasticity.

[0065] Dynamic oscillation characterizations are conducted on the HAP materials to characterize the viscoelastic properties, wherein a sample is deformed sinusoidally. The test is conducted via a stress sweep, wherein a constant frequency is applied with an increasing stress (amplitude), or conversely a frequency sweep, wherein a constant stress is applied with varied frequency. The measured strain of the elastic component of the material will be in phase with the imposed stress, whereas the viscous component of the material will be 90° out of phase. The $\tan \delta$ is the ratio of

the viscous to elastic components of the material, and characterizes the material as exhibiting more viscous or elastic properties. Thus, a material having a $\tan \delta$ of greater than 1 at a specific frequency would exhibit predominantly viscous behavior, and a $\tan \delta$ less than 1 would exhibit predominantly elastic behavior.

[0066] The HAP may be utilized as the sole retention/drainage aid. Alternatively, this polymer may be employed in combination with at least one flocculant, such as a conventional papermaking flocculent—e.g., a high MW cationic, anionic, or nonionic flocculent.

[0067] The method of the invention can be practiced using a papermaking apparatus or system as discussed herein. It is emphasized that the inventive method is not limited to this particular apparatus or system, which is only provided as a representative example of what can be employed.

[0068] As reviewed in *Handbook for Pulp and Paper Technologists* (G. A. Smook, TAPPI Press, Atlanta, Ga.), pulp components are usually metered into the machine stock chest at a consistency level between 2.8 and 3.2 wt %. The machine stock chest will usually contain the final mixture, although in some instances, small concentrations of additives may be added just prior to the headbox. The machine chest stock is usually circulated to a constant head tank (stuff box), which feeds the stock through a control valve (the basis weight valve) into the paper machine approach system.

[0069] The heart of the approach system is the fan pump which serves to mix the stock with the white water and deliver the blend to the headbox. Here the stock is combined with the circulating white water from the wire pit, and the consistency is reduced to the level required at the headbox (usually between about 0.5 wt % and about 1.0 wt % consistency).

[0070] The white water, which typically has a solids concentration of about 0.1 weight percent or less, is liquid from the dewatering of the pulp slurry on the papermaking wire that drains into the wire pit.

[0071] After the fan pump, the pulp slurry typically passes through a centrifugal cleaner, and then through a pressure screen, to a head box.

[0072] The centrifugal cleaner removes debris such as shives and slivers, and the pressure screen removes gross contamination and deflocs the fibers. The headbox serves to distribute the stock onto the earlier indicated endless moving papermaking wire or fabric; this may be a Fourdrinier wire or a twin wire former.

[0073] On the moving papermaking wire or fabric the slurry is dewatered; the resulting liquid is the white water as discussed above, draining from the slurry into the wire pit. This drainage forms the slurry into a sheet as it is carried on the wire or fabric to the press section.

[0074] Traveling through the press section, the sheet is pressed between rollers and thereby subjected to further dewatering. The sheet continues through the press section into a dryer section, wherein it is additionally dried. From the dryer section the sheet continues through a calender stack. In the calender stack it is pressed between metal rollers to reduce thickness and smooth the surface.

[0075] From this calender stack the sheet is wound onto a reel.

[0076] The resultant paper may also be surface coated with a sizing agent or coating material.

[0077] The materials utilized in the method of the invention include cellulosic pulp and at least one HAP. There can also be employed one or more additional materials, including at least one starch, at least one filler, at least one inorganic or organic coagulant, and at least one conventional flocculent.

[0078] Where a flocculant is employed, the flocculant and the HAP may be added simultaneously, or at different points in the method without an intermittent shear point, or at different points with an intermittent shear point between their respective additions. Preferably, the flocculant and the HAP are introduced into the method of the invention sequentially, i.e., at different points or times. The flocculant may be added before or after the HAP.

[0079] A shear may be affected to the stock between the addition of the flocculant and HAP when added sequentially. In an apparatus or system as discussed herein, high shear is effected at the fan pump, centrifugal cleaner, and pressure.

[0080] Consistent with the foregoing, the apparatus or system preferably is provided with suitable feed points for adding the previously discussed materials, such as the flocculant and the HAP. In this regard, the flocculant and/or the HAP may be added at a feed point before the fan pump (e.g., between the basis weight valve and the fan pump), and/or at a feed point before the centrifugal cleaner (e.g., between the fan pump and the centrifugal cleaner), and/or at a feed point before the pressure screen (e.g., between the centrifugal cleaner and the pressure screen).

[0081] With respect to feed points for the other materials, starch, filler, or coagulant may be added at numerous points within the process as is known to those skilled in the art.

[0082] The order in which the different materials are introduced into the method of the invention is not limited to that set forth in the preceding discussion, but will generally be based on practicality and performance for each specific application.

[0083] 3. Materials Employed

[0084] a. Cellulosic Pulp

[0085] 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.

[0086] b. Starch

[0087] Starch adds strength properties, particularly dry strength, to the cellulosic product obtained from the method of the invention. Particularly, starch increases interfiber bonding in the stock. Starch will also affect drainage properties.

[0088] Starches that may be used in the method of the invention include cationic and amphoteric starches. Suitable starches include those derived from corn, potato, wheat, rice, tapioca, and the like.

[0089] Cationicity is imparted by the introduction of cationic groups, and amphotericity by the further introduction of anionic groups. For instance, cationic starches may be obtained by reacting starch with tertiary amines or with quaternary ammonium compounds, e.g., dimethylaminoethanol and 3-chloro-2-hydroxypropyltrimethylammonium chloride. Cationic starches preferably have a cationic degree of substitution (D.S.)—i.e., the average number of cationic groups substituted for hydroxyl groups per anhydroglucose unit—of from about 0.01 to about 1.0, more preferably about 0.01 to about 0.10, more preferably about 0.02 to 0.04.

[0090] Amphoteric starches can be provided by the introduction of various different anionic groups. Preferred amphoteric starches are those with a net cationicity.

[0091] As an example, anionic phosphate groups can be introduced into cationic starches through reaction with phosphate salts or phosphate etherifying reagents. Where the cationic starch starting material is starch diethylaminoethyl ether, the amount of phosphate reagent employed in the modification preferably is that which will provide about 0.07-0.18 mole of anionic groups per mole of cationic groups.

[0092] Other amphoteric starches that may be used are those made by introduction of sulfosuccinate groups into cationic starches. This modification is accomplished by adding maleic acid half-ester groups to a cationic starch and reacting the maleate double bond with sodium bisulfite.

[0093] As yet additional examples, cationic starch can be etherified with 3-chloro-2-sulfopropionic acid, carboxyl groups can be introduced into starches by reaction with sodium chloroacetate or by hypochlorite oxidation, and propane sultone can be employed to treat cationic starches to provide amphotericity.

[0094] Further useful amphoteric starches can be obtained by xanthation of diethylaminoethyl- and 2-(hydroxypropyl)trimethylammonium starch ethers.

[0095] Yet additionally, the modification can be extended by the introduction of nonionic or hydroxyalkyl groups from treatment with ethylene oxide or propylene oxide.

[0096] Starch is preferably employed, in the method of the invention, in a proportion of from about 1 lb. per ton to about 100 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The starch concentration is more preferably from about 2.5 lbs. per ton to about 50 lbs. per ton, and still more preferably from about 5 lbs. per ton to about 25 lbs. per ton, of the pulp.

[0097] c. Filler

[0098] Filler provides optical properties to the cellulosic product. It provides opacity and brightness to the finished sheet, and improves its printing properties. Fillers which are suitable include calcium carbonate (both naturally occurring ground carbonate and synthetically produced precipitated carbonate), titanium oxide, talc, clay, and gypsum. The amount of filler employed can be that which results in a cellulosic product of up to about 50 weight percent filler, based on the dry weight of the pulp.

[0099] d. Coagulant

[0100] The coagulant is utilized in addition to the flocculant and HAP to enhance retention and drainage. The employed coagulant may be either inorganic or organic.

[0101] The most common inorganic coagulant is an alumina species. Suitable examples include technical grade aluminum sulfate (alum), polyaluminum chloride, polyhydroxy aluminum chloride, polyhydroxy aluminum sulfate, sodium aluminate, and the like.

[0102] The organic coagulant is typically a synthetic, polymeric material. Suitable examples include polyamines, poly(amido amines), polyDADMAC, polyethyleneimine, hydrolyzates and quaternized hydrolyzates of N-vinyl formamide polymers and copolymers, and the like.

[0103] The coagulant is preferably employed, in the method of the invention, in a proportion of from about 0.05 lb. per ton to about 50 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The coagulant concentration is more preferably from about 0.5 lbs. per ton to about 20 lbs. per ton, and still more preferably from about 1 lb. per ton to about 10 lbs. per ton, of the pulp.

[0104] e. Flocculant

[0105] Ionic flocculants conventional in the papermaking art are suitable as flocculants for the method of the present invention. Cationic, anionic, nonionic, and amphoteric flocculants—particularly, cationic, anionic, nonionic, and amphoteric polymers—can be used.

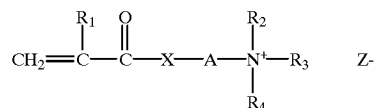
[0106] Polymers suitable as flocculants in the method of the invention include homopolymers of a nonionic ethylenically unsaturated monomer. Copolymers of monomers comprising two or more nonionic ethylenically unsaturated monomers can also be used, as can copolymers of monomers comprising at least one nonionic ethylenically unsaturated monomer and at least one cationic ethylenically unsaturated monomer and/or at least one anionic ethylenically unsaturated monomer.

[0107] The nonionic, cationic, and anionic ethylenically unsaturated monomers which may be employed are those discussed herein as being appropriate for the at least one HAP of the invention.

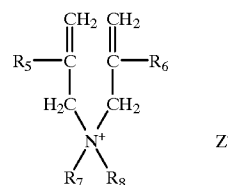
[0108] Suitable nonionic ethylenically unsaturated monomers include acrylamide; methacrylamide; N-alkylacrylamides, such as N-methylacrylamide; N,N-dialkylacrylamides, such as N,N-dimethylacrylamide; methyl acrylate; methyl methacrylate; acrylonitrile; N-vinyl methylacetamide; N-vinyl methyl formamide; vinyl acetate; N-vinyl pyrrolidone; hydroxyalkyl(meth) acrylates such as hydroxyethyl(meth) acrylate or hydroxypropyl(meth) acrylate; mixtures of any of the foregoing and the like. Of the foregoing, acrylamide, methacrylamide, and the N-alkylacrylamides are preferred, with acrylamide being particularly preferred.

[0109] Among the cationic ethylenically unsaturated monomers which may be used are diallylamine, the (meth)acrylates of dialkylaminoalkyl compounds, the (meth)acrylamides of dialkylaminoalkyl compounds, the N-vinylamine hydrolyzate of N-vinylformamide, and the salts and quaternaries thereof. The N,N-dialkylaminoalkyl acrylates and methacrylates, and their acid and quaternary salts, are pre-

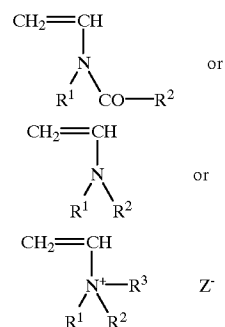
ferred, with the methyl chloride quaternary of N,N-dimethylaminoethylacrylate being particularly preferred. Further as to the cationic monomers, suitable examples include those of the following general formulae:



[0110] where R₁ is hydrogen or methyl, R₂ is hydrogen or lower alkyl of C₁ to C₄, R₃ and/or R₄ are hydrogen, alkyl of C₁ to C₁₂, aryl, or hydroxyethyl, and R₂ and R₃ or R₂ and R₄ can combine to form a cyclic ring containing one or more hetero atoms, Z is the conjugate base of an acid, X is oxygen or NR₁ wherein R₁ is as defined above, and A is an alkylene group of C₁ to C₂₂; or



[0111] where R₅ and R₆ are hydrogen or methyl, R₇ is hydrogen or alkyl of C₁ to C₁₂, and R₈ is hydrogen, alkyl of C₁ to C₁₂, benzyl, or hydroxyethyl; and Z is as defined above; or N-vinylformamides and the associated hydrolyzates as represented by recurring units of



[0112] where R¹, R² and R³ are each H or C₁ to C₃ alkyl, and Z is defined above.

[0113] Suitable anionic ethylenically unsaturated monomers include acrylic acid, methacrylic acid, and their salts; 2-acrylamido-2-methyl-propane sulfonate; sulfoethyl(meth)acrylate; vinylsulfonic acid; styrene sulfonic acid; and maleic and other dibasic acids and their salts. Acrylic acid, methacrylic acid and their salts are preferred, with the sodium and ammonium salts of acrylic acid being particularly preferred.

[0114] The monomers may be polymerized into polymer by a number of initiator systems, including free radical (thermal and redox methods), cationic, and anionic synthesis methods. The flocculant polymer may be prepared by a number of commercial means, including bulk polymerization, solution polymerization, dispersion polymerization, and emulsion/inverse emulsion polymerization. The resultant polymer may be provided to the end use in a number of physical forms, including aqueous solution, dry solid powder, dispersion, and emulsion form.

[0115] The flocculant may be non-ionic, cationic, anionic, or amphoteric. Non-ionic polymer flocculants will contain one or more of the previously described non-ionic monomers.

[0116] Cationic polymer flocculants will contain one or more of the cationic monomers described above. The level of total cationic monomer, based upon molar concentrations, will range from about 1 to about 99%, preferably from about 2 to about 50%, and still more preferably from about 5 to about 40 mole % cationic monomer, with the remaining monomer being one of the previously described non-ionic monomers.

[0117] Anionic polymer flocculants will contain one or more of the anionic monomers described above. The level of total anionic monomer, based upon molar concentrations, will range from about 1 to about 99%, preferably from about 2 to about 50%, and still more preferably from about 5 to about 40 mole % cationic monomer, with the remaining monomer being one of the previously described non-ionic monomers.

[0118] Amphoteric polymer flocculants will contain a combination of one or more of the described cationic and anionic monomers. Any combination of cationic and anionic monomer(s) are preferred, provided at least one cationic and one anionic monomer are utilized. The polymer may contain an excess of cationic monomer, an excess of anionic monomer, or equivalent amounts of both cationic and anionic monomers. The level of total ionic monomer, being the combined amount of both cationic and anionic monomers, based upon molar concentrations, will range from about 1 to about 99%, preferably from about 2 to about 80%, and still more preferably from about 5 to about 40 mole % cationic monomer, with the remaining monomer being one of the previously described non-ionic monomers.

[0119] The flocculant is preferably employed, in the method of the invention, in a proportion of from about 0.01 lb. per ton to about 10 lbs. per ton of cellulosic pulp, based upon active polymer weight and on the dry weight of the pulp. The concentration of flocculant is more preferably from about 0.05 lb. per ton to about 5 lbs. per ton, and still more preferably from about 0.1 lb. per ton to about 1 lb. per ton, of the pulp.

[0120] f. Hydrophobically Associative Polymer (HAP)

[0121] The invention comprises at least one HAP. Suitable HAPs of the invention include copolymers comprising at least one hydrophobic ethylenically unsaturated monomer with the proviso that the at least one hydrophobic ethylenically unsaturated monomer does not contain 2,4,6-tripheno-

ethyl benzene. These copolymers further include at least one nonionic ethylenically unsaturated monomer, and/or at least one cationic ethylenically unsaturated monomer, and/or at least one anionic ethylenically unsaturated monomer.

[0122] The indicated hydrophobic ethylenically unsaturated monomers include water-insoluble hydrophobic ethylenically unsaturated monomers. Further as to the hydrophobic ethylenically unsaturated monomers, they include ethylenically unsaturated monomers, particularly water-insoluble monomers and monomeric surfactants, having hydrophobic groups. The hydrophobic groups include hydrophobic organic groups, such as those having hydrophobicity comparable to one of the following: aliphatic hydrocarbon groups having at least four carbons such as C₄ to C₂₀ alkyls and cycloalkyls; polynuclear aromatic hydrocarbon groups such as benzyls, substituted benzyls and naphthyls with the proviso that the substituted benzyl group is not 2,4,6-triphenoethyl benzene; 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 4 carbons or more per hydrocarbon group, such as the C₄-C₂₀ alkyl groups or those having at least 4 carbons or more per perfluorocarbon group, such as the C₄F₉-C₂₀F₄₁. Particularly preferred are the C₈-C₂₀ alkyl groups.

[0123] Suitable hydrocarbon group-containing ethylenically unsaturated monomers include the esters or amides of the C₄ and higher alkyl groups.

[0124] Particular suitable esters include dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, nonyl- α -phenyl acrylate, nonyl- α -phenyl methacrylate, dodecyl- α -phenyl acrylate, and dodecyl- α -phenyl methacrylate.

[0125] The C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid are preferred. Of these, dodecyl acrylate and methacrylate are particularly preferred.

[0126] Also the following hydrocarbon group-containing ethylenically unsaturated monomers may be used:

[0127] N-alkyl ethylenically unsaturated amides, such as N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl acrylamide and similar derivatives thereof;

[0128] α -olefins, such as 1-octene, 1-decene, 1-dodecene, and 1-hexadecene;

[0129] vinyl esters wherein the ester has at least eight carbons, such as vinyl laurate and vinyl stearate;

[0130] vinyl ethers, such as dodecyl vinyl ether and hexadecyl vinyl ether;

[0131] N-vinyl amides, such as N-vinyl lauramide and N-vinyl stearamide;

[0132] -alkylstyrenes, such as t-butyl styrene;

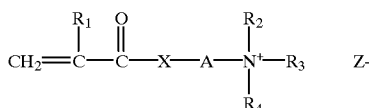
[0133] -alkyl polyethyleneglycol (meth)acrylates such as laurylpolyethoxy(23) methacrylate; and

[0134] N-alkyl ethylenically unsaturated cationic monomers such as the C₁₀-C₂₀, alkyl halide quaternary salts of methyldiallyamine, N,N-dimethylaminoalkyl(meth)acrylates, and N,N-dialkylaminoalkyl(meth)acrylamides.

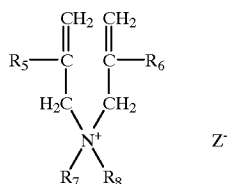
[0135] Suitable nonionic ethylenically unsaturated monomers include acrylamide; methacrylamide; N-alkylacrylamides, such as N-methylacrylamide; N,N-dialkylacrylamides, such as N,N-dimethylacrylamide; methyl acrylate; methyl methacrylate; acrylonitrile; N-vinyl methylacetamide; N-vinyl methyl formamide; vinyl acetate; N-vinyl pyrrolidone; mixtures of any of the foregoing and the like. Of the foregoing, acrylamide, methacrylamide, and the N-alkylacrylamides are preferred, with acrylamide being particularly preferred.

[0136] Among the cationic ethylenically unsaturated monomers which may be used are diallylamine, the (meth)acrylates of dialkylaminoalkyl compounds, the (meth)acrylamides of dialkylaminoalkyl compounds, the N-vinylamine hydrolyzate of N-vinylformamide, and the salts and quaternaries thereof. The N,N-dialkylaminoalkyl acrylates and methacrylates, and their acid and quaternary salts, are preferred, with the methyl chloride quaternary of N,N-dimethylaminoethylacrylate being particularly preferred.

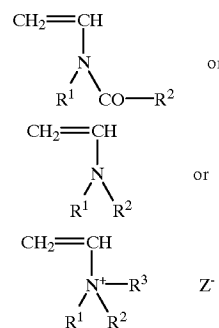
[0137] Further as to the cationic monomers, suitable examples include those of the following general formulae:



[0138] where R₁ is hydrogen or methyl; R₂, R₃ and R₄ are hydrogen, alkyl of C₁ to C₃, or hydroxyethyl; and R₂ and R₃ or R₂ and R₄ can be combined to form a cyclic ring containing one or more hetero atoms; Z is the conjugate base of an acid; X is oxygen or NR₁ wherein R₁ is as defined above; and A is an alkylene group of C₁ to C₁₂; or



[0139] where R₅ and R₆ are hydrogen or methyl, R₇ and R₈ are hydrogen, alkyl of C₁ to C₃, or hydroxyethyl; and Z is as defined above; or N-vinylformamides and the associated hydrolyzates as represented by recurring units of



[0140] where R¹, R² and R³ are each H or C₁ to C₃ alkyl, and Z is defined above.

[0141] Suitable anionic ethylenically unsaturated monomers include acrylic acid, methacrylic acid, and their salts; 2-acrylamido-2-methyl-propane sulfonate; sulfoethyl(meth)acrylate; vinylsulfonic acid; styrene sulfonic acid; and maleic and other dibasic acids and their salts. Acrylic acid, methacrylic acid and their salts are preferred, with the sodium and ammonium salts of acrylic acid being particularly preferred.

[0142] As a matter of preference, the proportion of hydrophobic ethylenically unsaturated monomer in the HAP is within a range which renders the polymer hydrophobically associative—i.e., the hydrophobic monomer concentration is low enough so that the polymer is still water soluble or dispersible, but sufficient to provide the associative property as discussed herein. In this regard, the at least one HAP preferably comprises about 0.001 mole percent to about 10 mole percent—more preferably about 0.01 mole percent to about 5 mole percent, and still more preferably about 0.1 mole percent to about 2.0 mole percent—of the at least one hydrophobic ethylenically unsaturated monomer.

[0143] The HAPs used in the invention include anionic, nonionic, and cationic and amphoteric copolymers. Of these, the anionic copolymers are preferred.

[0144] The anionic copolymers comprise at least one hydrophobic ethylenically unsaturated monomer and at least one anionic ethylenically unsaturated monomer. Preferably, the anionic copolymers further comprise at least one nonionic ethylenically unsaturated monomer. Particularly preferred are the terpolymers consisting of, or consisting essentially of, or substantially of, at least one hydrophobic ethylenically unsaturated monomer, at least one anionic ethylenically unsaturated monomer, and at least one nonionic ethylenically unsaturated monomer.

[0145] For the anionic copolymers the preferred hydrophobic ethylenically unsaturated monomers are the hydrocarbon esters of α,β-ethylenically unsaturated carboxylic acids and their salts, with dodecyl acrylate and dodecyl methacrylate being particularly preferred. Preferred nonionic ethylenically unsaturated monomers are acrylamide and methacrylamide. Preferred anionic ethylenically unsaturated monomers are acrylic acid and methacrylic acid.

[0146] The anionic copolymers preferably comprise about 0.001 mole percent to about 10 mole percent hydrophobic ethylenically unsaturated monomer, about 1 mole percent to about 99.999 mole percent nonionic ethylenically unsaturated monomer, and about 1 mole percent to about 99.999 mole percent of the at least one anionic ethylenically unsaturated monomer. More preferably, they comprise about 0.01 mole percent to about 5 mole percent of the at least one hydrophobic ethylenically unsaturated monomer, about 10 mole percent to about 90 mole percent of the at least one nonionic ethylenically unsaturated monomer, and about 10 mole percent to about 90 mole percent of the at least one anionic ethylenically unsaturated monomer. Still more preferably, they comprise about 0.1 mole percent to about 2.0 mole percent of the at least one hydrophobic ethylenically unsaturated monomer, about 50 mole percent to about 70 mole percent of the at least one nonionic ethylenically unsaturated monomer, and about 30 mole percent to about 70 mole percent of the at least one anionic ethylenically unsaturated monomer.

[0147] The monomers may be polymerized into a HAP polymer by a number of initiator systems, including free radical (thermal and redox methods), cationic, and anionic synthesis methods. The HAP may be prepared by a number of commercial means, including bulk polymerization, solution polymerization, micellar solution polymerization, dispersion polymerization, and emulsion/inverse emulsion polymerization. The resultant polymer may be provided to the end use in a number of physical forms, including aqueous solution, dry solid powder, dispersion, and emulsion form.

[0148] The HAP is preferably employed, in the method of the invention, in a proportion of from about 0.01 lb. per ton to about 10 lbs. per ton of cellulosic pulp, based on the dry weight of the pulp. The concentration of HAP is more preferably from about 0.05 lb. per ton to about 5 lbs. per ton, and still more preferably from about 0.1 lb. per ton to about 1 lb. per ton, of the pulp.

[0149] g. Further Additives

[0150] The method of the invention may yet additionally include conventional additives employed in their usual amounts for their usual purposes. Suitable examples include sizing, promoters, strength agents, dye fixatives, polymeric coagulants, and the like. The produced paper may also be surface treated with a surface size or coating material.

[0151] 4. Composition of the Invention

[0152] A factor affecting the concentration of HAP in the cellulosic composition of the invention is the proportion of the polymer added during the preparation method. The cellulosic composition of the invention—which preferably is a cellulosic sheet, and more preferably is paperboard or paper—preferably comprises about 0.01 to about 10 weight percent—more preferably about 0.05 weight percent to about 5 weight percent, and still more preferably about 0.1 weight percent to about 1 weight percent—of the HAP, based on the dry weight of the composition.

EXPERIMENTAL SECTION

[0153] The invention is illustrated by the following procedures and tests; these are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention. Unless stated otherwise, all percentages, parts, etc. are by weight.

[0154] 1. Preparation of the Flocculant HAPs of the Invention and Controls

[0155] a.) Solution Polymerization

[0156] HAPs used in the invention, the anionic copolymers II, III, and V to VII are prepared from acrylamide (AM), acrylic acid (AA), and lauryl acrylate (LA). Control polymers, the anionic copolymers I and IV, are prepared without the hydrophobically modified monomer lauryl acrylate—i.e., from acrylamide and acrylic acid alone.

[0157] Polymers I-VII are all prepared by solution polymerization. The relative proportions of monomers used in each instance are set forth below.

TABLE I

Solution Polymer Sample Description		
Polymer	Monomers	Feed Ratio (mole %)
I (control)	AA/AM	45/55
II	AA/AM/LA	45/54/1
III	AA/AM/LA	45/54/1
IV (control)	AA/AM	30/70
V	AA/AM/LA	30/69.5/0.5
VI	AA/AM/LA	30/69/1
VII	AA/AM/LA	30/68/2

[0158] In the case of Polymers II and III, a solution of 2.75 parts of acrylamide, 0.17 parts (1 mol % of the monomers) of lauryl acrylate, 2.25 parts of acrylic acid, 1 part of the nonionic surfactant (Tergitol 15-S-9), and 100 parts of deionized water is deoxygenated under stirring at room temperature by sparging with nitrogen for 45 minutes. 0.5 part of a 2 mg KBrO_3 solution is added and 10 parts of 0.03% of $\text{Na}_2\text{S}_2\text{O}_5$ is injected by a syringe pump over 60 minutes. The copolymer is obtained by the precipitation of the polymerization solution in acetone and dried under vacuum at 50° C. overnight.

[0159] Polymers V, VI and VII are prepared in the same manner, except for the ratio of the monomers. For Polymer V, the monomer ratio is 3.4 parts of acrylamide, 0.1 part (0.5 mol % of the monomers) of lauryl acrylate, and 1.5 parts of acrylic acid. For Polymer VI, the monomer ratio is 3.4 parts of acrylamide, 0.19 parts (1 mol % of the monomers) of lauryl acrylate, and 1.5 parts of acrylic acid. For Polymer VII, the monomer ratio is 3.4 parts of acrylamide, 0.38 parts (2 mol % of the monomers) of lauryl acrylate, and 1.5 parts of acrylic acid.

[0160] Polymer I is prepared using the same method and proportions as with Polymers II and III, except without the lauryl acrylate. Polymer IV is prepared in the same manner as Polymer I, except that for Polymer IV the monomer ratio is 3.5 parts of acrylamide and 1.5 parts of acrylic acid.

[0161] For each of Polymers I, II, and III, the resulting dried product is redissolved in deionized water to produce a 0.5% polymer solution which is subjected to viscosity characterization.

[0162] b). Dispersion Polymerization

[0163] Hydrophobic associative polymers are prepared via dispersion polymerization.

TABLE 2

Brine Dispersion Sample Description		
Polymer	Monomer	Feed Ratio (mole %)
VIII (control)	AA/AM	50/50
IX	AA/AM/LMA	49.9/50/0.1
X	AA/AM/LMA	49.8/50/0.2
XI	AA/AM/LA	50/49.75/0.25
XII	AA/AM/LA	50/49.5/0.5

LMA - Lauryl methacrylate

LA - Lauryl acrylate

[0164] 2. Viscosity Characterization

[0165] a). Solution Polymerization

[0166] The viscosity of each 0.5% solution is measured by Brookfield viscometer at 12 rpm and room temperature. The results are set forth in Table 3 below. The molecular weights of the HAPs II and III, and of the non-associative Polymer I, are assumed to be similar, because of their being prepared under substantially identical synthesis conditions. The 20 fold increase in 0.5% solution viscosity of the HAPs II and III over the Polymer I control sample is a qualitative indication of the incorporation of the hydrophobic monomer in Polymers II and III. The extremely high 0.5% solution viscosity for Polymers II and III also indicates that the HAPs of the invention are strongly associative in aqueous solution.

TABLE 3

Viscosity Characterization		
Samples	Monomers	0.5% Solution Viscosity (cP)
I (control)	AA/AM	600
II	AA/AM/LA	14,000
III	AA/AM/LA	12,000

[0167] Viscosity and rheological characterizations are further conducted on Samples IV through VII to demonstrate the associative properties of the modified samples compared to the unmodified control. The described studies are conducted at 0.5% aqueous solution. As is exhibited previously in Table 3, Brookfield viscosity at 12 rpm is conducted on the samples, exhibiting a significant increase in apparent viscosity with increased levels of hydrophobe. The highest level of hydrophobe exhibits a 10 fold increase in Brookfield Viscosity due to associative interactions. Additional studies are also conducted with a Haake RS-75 controlled stress rheometer equipped with a cone and plate geometry, with a 60 mm diameter cone and a fixed angle of 2 degrees. The apparent viscosity of the 0.5% solid content polymer

samples is determined at a constant shear rate of 10 sec⁻¹, with similar results observed as with the Brookfield viscometer, in that a 10 fold increase in viscosity is observed with the highest level of hydrophobe, indicating strong associative behavior. A stress sweep is conducted with the instrument in dynamic stress oscillation mode, at a constant 1 Hz frequency, and a stress range of 0.1 to 10.0 Pa in 20 logarithmic steps. The G' storage modulus is assigned as the equilibrium value in the linear viscoelastic region, and is defined as:

$$G' = (\tau_0 / \gamma_0) \cos \delta$$

[0168] where τ_0 is the stress amplitude, γ_0 is the maximum strain amplitude, and δ is the phase angle shift between the stress and resultant strain. The G' storage modulus is also referred to as the gel modulus, and is taken as an indication of the degree and strength of the network structure, as determined by the inter-/intra-molecular hydrophobic associations. At equivalent applied stress, materials with a higher G' value will strain or deform less, thus exhibiting a stronger gel complex or network structure. The data demonstrates a linear relationship between hydrophobe concentration and G' storage modulus, with the modulus increasing with increased level of hydrophobe, and the highest G' storage modulus for the highest level of hydrophobic substitution. The unmodified Polymer IV exhibits a storage modulus of 2 Pa, while the modified Polymer VII containing 2 mole % lauryl acrylate exhibits a storage modulus of 25.6 Pa.

[0169] A frequency sweep in dynamic oscillation mode is subsequently conducted with the instrument in dynamic oscillation mode, at a constant stress of 0.1 Pa, and a frequency range of 0.0068 Hz to 10 Hz with 3 readings per frequency decade. The tan δ is the ratio of the loss (viscous) modulus to storage (elastic) modulus, determined according to:

$$\tan \delta = \text{loss modulus} / \text{storage modulus} = G'' / G'$$

[0170] Materials that possess a higher tan δ value exhibit more viscous properties, while a lower tan δ will indicate more elastic properties. At a low frequency such as 0.0068 Hz, the rate of stress on the sample will permit a linear polymer to relax, and exhibit a viscous type response, or a higher tan δ . Polymers comprised either of a chemical or physical network exhibit significant structure of the polymer chains. These network structured materials are mechanically stable and do not relax within the time frame or frequency of the experiment. These materials exhibit lower values of tan δ , and thus are more elastic. As shown in Table 4, a tan δ at 0.0068 Hz of 20 is observed for the unmodified control polymer, while the highest level of hydrophobe provides a tan δ of 0.224. Lower levels of tan δ are observed with higher levels of hydrophobic substitution over a wide range of frequencies, up to 6.8 Hz. This clearly demonstrates the strong associative behavior of the HAP, and it is consistent with the viscosity data discussed above.

TABLE 4

Controlled Stress Rheometer Dynamic Oscillation Studies						
Poly- mer	Monomer	Feed Ratio (mole soln %)	Charge Density meq/g	Shear	Stress	Fre- quency Sweep tan δ , 0068 Hz
				Brook- field rpm 0.5% soln vis, mPas	rate = Sweep G" Storage Modu- lus, Pa	
IV (control)	AA/AM	30/70	650	1070	2	19.9
V	AA/AM/LA	30/69.5/ 0.5	1700	2350	2.3	1.1
VI	AA/AM/LA	30/69/1	8500	16400	12	0363
VII	AA/AM/LA	30/68/2	7000	10500	25.6	0.224

[0171] b). Dispersion Polymerization

[0172] The dispersion polymers are characterized according to equivalent methods as described in the solution polymerization polymers. The data presented in Table 5 demonstrates similar results as with the solution polymerization products. The 0.5% solution apparent viscosity is observed to increase with the introduction of the hydrophobic monomer. A stress sweep study in dynamic oscillation mode demonstrates a G' storage modulus increase with samples IX and XI compared to the unmodified control sample VIII. A frequency sweep study in dynamic oscillation mode demonstrates a low tan δ for the hydrophobic associative polymer compared to the unmodified control.

TABLE 5

Controlled Stress Rheometer Dynamic Oscillation Studies						
Poly- mer	Monomer	Feed Ratio (mole %)	Charge Density meq/g	Shear	Stress	Fre- quency Sweep tan δ .0068 Hz
				Brook- field rpm 0.5% soln vis, mPas	rate = Sweep G" Storage Modu- lus, Pa	
VIII (control)	AM/AA	50/50	6.4	530	3.39	7.23
IX	AM/AA/ LMA	50/49.9/ 0.1	7.5	1230	10.9	0.92
X	AM/AA/ LMA	50/49.8/ 0.2	7.0	510	Non- linear	n/a
XI	AA/AM/LA	50/ 49.75/ 0.25	7.6	1270	10.9	0.72
XII	AA/AM/LA	50/49.5/ 0.5	7.3	410	Non- linear	n/a

LA - Lauryl acrylate

LMA - Lauryl methacrylate

[0173] The dilute solution viscosity properties of the Table 5 HAP samples were determined in aqueous solutions at various concentrations of NaCl and compared to Polyflex CP.3, a commercial polyacrylamide drainage aid (Cytac Industries, Inc., West Patterson, N.J.) and Polymer E, a commercial high MW anionic polyacrylamide flocculent. The data are presented in Table 5.1. As discussed in *Introduction to Physical Polymer Science* by L. H. Sperling (Wiley Interscience, 1992), the dilute solution properties provide a relative indication of polymer molecular weight. In this experiment, the solvent viscosity η_0 is compared to the polymer solution viscosity η . The relative viscosity is the unitless ratio of the two:

$$\eta_{rel} = \eta / \eta_0$$

[0174] and the specific viscosity is relative viscosity minus one:

$$\eta_{sp} = \eta_{rel} - 1$$

[0175] The reduced specific viscosity, referred to hereafter as the RSV, is the specific viscosity divided by the polymer concentration (C) in gram per deciliter units:

$$RSV = \eta_{sp} / C$$

[0176] The units for RSV are deciliter per gram (dL/g), and as such describe the hydrodynamic volume (HDV) of a polymer in solution. Thus a higher RSV indicates a large HDV in solution, and a higher MW when comparing conventional polymers. The experiment is conducted in the dilute regime such that no polymer coil overlap is occurring. The RSV values can be determined by capillary or rotational viscometer methods by measuring the respective efflux time or apparent viscosity of both the solvent and the polymer solutions. The data described in Table 5.1 were determined with a Brookfield rotational viscometer equipped with an ultra-low (UL) adapter, capable of determining the viscosity of low viscosity solutions. The data demonstrate the effect on polyelectrolyte RSV with varying salt concentrations, as is well known to those skilled in the art. The inventive HAP products demonstrate a higher RSV in 1 M NaCl that contains an additional 0.1% nonylphenol ethoxylate (NPE) surfactant than in 1 M NaCl only. This phenomena, which shall be referred to as "RSV Ratio", is a dilute solution property specific to associative polymers containing hydrophobes, and does not occur in linear, cross-linked, or branched polymers. The RSV Ratio is observed to increase dramatically with higher levels of hydrophobic monomer, and does not occur in the control polymer, Polyflex CP.3, or Polymer E. This phenomena is well established in the literature, and is explained as a binding of the hydrophobic domains with the surfactant, thus providing an increase in dilute solution viscosity or RSV.

TABLE 5.1

Dilute Solution RSV Determinations							
Polymer	Monomer	Feed Ratio (mole %)	RSV - DI Water dL/g	RSV - 0.01M NaCl - dL/g	RSV - 1M NaCl - dL/g	RSV - 1M NaCl + 0.1% NPE	Ratio - 1M NaCl: 1M NaCl + 0.1% NPE
VIII (control)	AM/AA	50/50	730	113	21	23	1.1
IX	AM/AA/LMA	50/49.9/0.1	990	106	12	20	1.7
X	AM/AA/LMA	50/49.8/0.2	700	23	2	15	1.5
XI	AA/AM/LA	50/49.75/0.25	930	128	16	24	7.5
XII	AA/AM/LA	50/49.5/0.5	650	34	4	17	4.3
Polyflex CP.3	AM/AA/**	40/60/**	580	47	13	13	1.0
Polymer E	AM/AA	50/50	1216	184	44	44	1.0
[Polymer Concentration]	dL/g		.001	.005	.025	.025	

LA - Lauryl acrylate

LMA - Lauryl methacrylate

NPE - nonylphenol ethoxylate surfactant

**Polyflex CP.3 is crosslinked at an unknown level.

[0177] 3. Retention and Drainage Tests

[0178] A first series of Britt jar retention tests and Canadian Standard Freeness (CSF) drainage tests are conducted to compare the performance of the HAPs of the invention, with those of the following: a non-hydrophobic associative polymer; a conventional anionic polyacrylamide flocculant; and inorganic and organic drainage aids commonly referred to within the industry as "microparticles" or "micropolymerers".

[0179] The Britt jar (Paper Research Materials, Inc., Gig Harbor, Wash.) retention test 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 μ screen in the bottom plate is utilized.

[0180] The CSF device (Lorentzen & Wettre, Code 30, Stockholm, Sweden) utilized to determine relative drainage rate or dewatering rate also is known in the art (TAPPI Test Procedure T-227). The CSF device comprises a drainage chamber and a rate measuring funnel, both mounted on a suitable support. The drainage chamber is cylindrical, fitted with a perforated screen plate and a hinged plate on the bottom, and with a vacuum tight hinged lid on the top. The rate measuring funnel is equipped with a bottom orifice and a side, overflow orifice.

[0181] The CSF test is conducted by placing 1 liter of furnish, typically at 0.30% consistency, in the drainage chamber, closing the top lid, and then immediately opening the bottom plate. The water is allowed to drain freely into the rate measuring funnel; water flow which exceeds that determined by the bottom orifice will overflow through the side orifice and is collected in a graduated cylinder. The values generated are described in millimeters (mls) of filtrate; higher quantitative values represent higher levels of dewatering.

[0182] The furnish employed in this first series of tests is a synthetic alkaline furnish. This furnish is prepared from hardwood and 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, Wis.) These pulps are then added to an aqueous medium.

[0183] 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 representative alkalinity and a total conductivity.

[0184] To prepare the furnish, the hardwood and softwood are dispersed into the aqueous medium at typical weight ratios of hardwood and softwood. 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 finish comprising 80% fiber and 20% PCC filler.

[0185] This first series of tests is conducted with the following: Polymer II, a hydrophobically associative anionic polyacrylamide of the invention as discussed herein; Polymer I, an unmodified anionic polyacrylamide control polymer as discussed herein; Polymer E, a high MW commercial anionic flocculant; Polyflex CP.3, a commercial polyacrylamide drainage aid (Cytec Industries, Inc., West Patterson, N.J.); and bentonite clay, also commonly employed in the industry as a drainage and retention aid.

[0186] The Britt jar retention tests in this first series are conducted with 500 mls of the synthetic furnish, having a typical solids concentration of 0.5%. The test is conducted at a constant rpm speed according to the following parameters, consistent with the sequence set forth in Table 2: add starch, mix; add alum, mix; add polymer flocculant, mix; add drainage aid, mix; obtain filtrate.

[0187] The cationic potato starch utilized is Stalok 600 (A. E. Staley, Decatur, Ill.), and the alum is aluminum sulfate-octadecahydrate available as a 50% solution (Delta Chemical Corporation, Baltimore, Md.). The cationic flocculant

utilized, referred to as CPAM-P, is a 90/10 mole % acrylamide/N,N-dimethylaminoethylacrylate methyl chloride quaternized; this material is commercially available as a self-inverting water-in-oil emulsion.

[0188] The retention values reported in Table 2 are fines retention where the total fines in the furnish is first determined by washing 500 mls of furnish with 10 liters of water under mixing conditions to remove all the fine particles, defined as particles smaller than the Britt jar 76 μ screen. The fines retention for each treatment is then determined by draining 100 mls of filtrate after the described addition sequence, then filtering the filtrate through a pre-weighed 1.5 μ filter paper. The fines retention are calculated according to the following equation:

$$\% \text{ Fines retention} = (\text{filtrate wt} - \text{fines wt}) / \text{filtrate wt}$$

[0189] where the filtrate and fines weight are both normalized to 100 mls. Retention values represent the average of 2 replicate runs.

[0190] The CSF drainage tests are conducted with 1 liter of the furnish at a solids concentration of 0.30%. The furnish is prepared for the described treatment externally from the CSF device, utilizing equivalent speeds and mixing times as described for the Britt jar tests, in a square beaker to provide turbulent mixing. Upon completion of the addition of the additives and the mixing sequence, the treated furnish is poured into the top of the CSF device and the test is conducted.

[0191] In both Britt jar retention and CSF drainage tests, higher quantitative values indicate higher activity and a more desired response.

[0192] The data set forth in Table 6 illustrates the superior activity provided by Polymer II of the invention, as compared to the results obtained with unmodified control Polymer I and the conventional anionic flocculant Polymer E. Further, the polymer of the invention provides activity equivalent to that of bentonite clay and approaching that of Polyflex CP.3. The described material dosages are all based upon product actives, unless noted otherwise.

TABLE 6

ADD #1	lbs./ton (active)	ADD #2	lbs./ton (active)	Polymer	lbs./ton (active)	Drainage Aid	Lbs./ton (active)	Avg. % Ret	CSF mls
Cationic Potato Starch	10	Alum	5	none				27 29	395
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	none	0	48 43	380
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	Polymer II	0.75	69 54	620
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	Polymer I	0.75	50 46	535
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	Polymer E	0.75	53 16	540
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	Polyflex CP.3	0.75	77 85	650
Cationic Potato Starch	10	alum	5	CPAM-P Flocculant	0.5	Bentolite HS	4	64 72	600

[0193] A series of retention and drainage tests are conducted utilizing a pulsed drainage device (PDD). The test substrate, test conditions, and associated chemical additives are identical to those utilized in Table 6.

[0194] The PDD is equipped with a rotating hydrofoil, and vacuum capability underneath a wire screen. It is an instrument developed internally (described in U.S. Pat. No. 5,314,581) as a reasonable simulation of the actual retention, drainage, and sheet formation operations. During the opera-

tion of the experiment, a vacuum is applied to the fibrous slurry to assist in the formation of a fibrous mat, and the vacuum is continued until a steady state equilibrium vacuum is achieved.

[0195] A variety of measurements can be taken with use of the PDD. For instance, the PDD can be used in determining first pass retention, peak vacuum, equilibrium vacuum, peak to equilibrium vacuum ratio (PEVR), and vacuum drainage time.

[0196] The first pass fines retention is determined by mass balance calculations involving the weight of the final sheet, the total mass introduced into the PDD, and the total fines fraction of the stock which is defined as the fraction of the stock that has a particle size less than 76 μ . As with Britt jar fines retention, higher values indicate the desired response.

[0197] The peak vacuum is the total vacuum required during mat formation until air is drawn through the formed mat and the vacuum is disrupted. Equilibrium vacuum is the steady state vacuum drawn through the formed sheet. Both peak vacuum and equilibrium vacuum are measured in inches of Hg. A lower quantitative value for the peak vacuum indicates a fibrous matrix that is easier to dewater.

[0198] The peak to equilibrium vacuum ratio (PEVR) is the unitless ratio of these two outputs. Studies have demonstrated that this parameter is useful as an indication of sheet formation, in that lower PEVR values indicate more desirable or more uniform sheet formation.

[0199] The vacuum drainage time is the time to peak vacuum, and is measured by the instrument in time units of seconds. It is believed this response is similar to the wet-line on a paper machine, which is the point where the water has drained sufficiently such that the sheet has lost its sheen or visible free water. The wet line position is commonly monitored as an indication of papermachine drainage. The desired responses for the vacuum drainage parameters are reduced (low) values, indicating improved drainage.

[0200] The second series of drainage tests, utilizing the PDD, is taken with the same drainage aids as the first series,

except for the absence of bentonite. The associated starch, alum, and cationic flocculant are as described previously. The results in Table 7 set forth the values obtained for the above measurements from taking the PDD measurements.

[0201] These results demonstrate that Polymer II of the invention provides a definitive drainage dosage response. Specifically, as the dosage is increased, the gravity drainage, the peak vacuum, and the vacuum drainage times improve accordingly.

[0202] It is noted that unmodified control Polymer I and the conventional flocculant Polymer E do not exhibit a dosage response. In this regard, as the dosage of these polymers is increased, the retention and associated drainage responses do not increase or decrease.

[0203] The improved drainage activity of Polymer II, as compared to that of control Polymer I and Polymer E, is also clearly shown by the Table 7 data. Polymer II provides higher fines retention than Polyflex CP.3 and approaches the drainage activity of Polyflex CP.3, as 1.0 lb./ton of Polymer II provides about equal drainage to 0.5 lbs./ton of Polyflex CP.3. It is noted that at these equal drainage times, the Polymer II provides lower PEVR values than Polyflex CP.3, an indication of improved sheet uniformity or formation.

[0204] A series of Britt jar retention and CSF tests is conducted with the following: Polymer III, hydrophobically associative anionic polyacrylamide of the invention as discussed herein; Polymers V-VII, hydrophobically associative polymers of the invention, exhibiting sequentially increased levels of hydrophobic modification; Polymer IV, an unmodified anionic polyacrylamide control polymer as discussed herein; Polymer E; and Polyflex CP.3. The tests are conducted according to the methods previously described. The data demonstrates the superior activity of the invention provided by Polymer III and Polymer VII, compared to the unmodified control Polymer IV. Increased retention and drainage activity are observed with increased level of hydrophobic substitution, with Polymer VII approaching the activity of Polyflex CP.3. The data is set forth in Table 8.

TABLE 7

10 Lbs./Ton Cationic Potato Starch + 5 Lbs./Ton Aluminum Sulfate + 0.5 Lbs./Ton CPAM-P Flocculant + Drainage Aid	DOSAGE (Lbs./T)	% First Pass Fines Retention	Gravity Drainage Time - seconds (mass measurement)	VACUUM Equilibrium. (in Hg)	PEAK VACUUM (in Hg)	Peak to Equilibrium Vacuum Ratio	Vacuum Drainage Time- seconds (Vacuum Time)
No Drainage Aid	0	89.09%	3.25	3.61	5.15	1.43	1.028
Polyflex CP.3	0.5	93.47%	3.04	2.97	4.44	1.49	0.679
Polyflex CP.3	0.75	95.10%	2.99	2.71	4.07	1.50	0.622
Polyflex CP.3	1	95.37%	3.01	2.65	4.01	1.51	0.608
Polymer I	0.5	92.34%	3.16	3.53	4.88	1.38	0.798
Polymer I	0.75	91.34%	3.18	3.53	4.81	1.36	0.801
Polymer I	1	94.74%	3.13	3.52	4.81	1.37	0.778
Polymer II	0.5	96.05%	3.09	3.27	4.66	1.42	0.731
Polymer II	0.75	95.83%	3.05	3.10	4.53	1.46	0.685
Polymer II	1	95.64%	2.91	3.01	4.43	1.47	0.673
Polymer E	0.5	93.31%	3.14	3.50	4.81	1.37	0.793
Polymer E	0.75	92.20%	3.18	3.43	4.78	1.39	0.786
Polymer E	1	94.21%	4.67	3.43	4.83	1.41	0.792

TABLE 8

Add #1	lbs./ton (active)	Add #2	lbs./ton (active)	Add #3	lbs./ton (active)	Drainage Aid	lbs./ton (active)	Avg. Ret.	CSF
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	some	0	51.4	100
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polyflex CP.3	0.75	77.5	510
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer E	0.75	19.5	530
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer IV	0.75	12.0	510
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer V	0.75	12.1	505
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer VI	0.75	55.4	515
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer VII	0.75	66.3	585
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer III	0.75	69.0	610

[0205] Another series of retention and drainage tests is conducted like the second series, with the PDD. The conditions and material are the same as employed for previous series, except that the drainage aids are as follows: Polymer III of the invention and Polyflex CP.3, as discussed herein; Polymer M, a commercially available high MW polyacrylamide emulsion flocculant; and bentonite clay.

[0206] The polymeric materials are evaluated at 0.5, 0.75, and 1.0 lbs./ton active polymer, while the bentonite clay is evaluated at 2, 4, and 6 lbs./ton, in accordance with typically utilized mill dosage levels. The results are set forth in Table 9.

[0207] The Table 9 data illustrates the activity of the polymer of the invention. Polyflex CP.3, bentonite clay, and Polymer III all exhibit positive dose response activity, while Polymer M is not dosage active. The Polymer III provides equal to greater retention and drainage activity as compared with bentonite clay.

[0208] Further as to the comparative activity shown in Table 9, Polymer M provides retention and drainage equal to that of Polymer III, but at distinctly higher PEVR; this reduction in sheet uniformity/formation at equal drainage is undesirable. The drainage activity of Polymer III approaches that of Polyflex CP.3, as 1.0 lb./ton of Polymer III approaches the drainage of 0.5 lb./ton Polyflex CP.3. It is again noted that at these equal drainage times, the PEVR of the polymer of the invention is lower than that of Polyflex CP.3, which is an indication of improved sheet uniformity or formation.

TABLE 9

10 Lbs/Ton Cationic Potato Starch + 5 Lbs./Ton Aluminum Sulfate - 0.5 Lbs./Ton CPAM-P Flocculant + Drainage Aid	DOSAGE (Lbs/T)	% First Pass Fines Retention	Gravity Drainage Time - seconds (mass measurement)	VACUUM Equilibrium (in Hg)	PEAK VACUUM (in Hg)	Peak to Equilibrium Vacuum Ratio	Vacuum Drainage Time - seconds (Vacuum Time)
None	0	87 60%	3 37	3 42	4 97	1 455	0 880
Polyflex CP 3	0 5	96 42%	3 17	2 77	4 05	1 465	0 627
Polyflex CP 3	0 75	98 81%	3 30	2 61	3 84	1 472	0 577
Polyflex CP 3	1	97 65%	3 18	2 49	3 70	1 486	0 515
Polymer III	0 5	95 39%	3 28	3 00	4 32	1 440	0 672
Polymer III	0 75	86 26%	3 09	2 98	4 29	1 442	0 662
Polymer III	1	95 54%	3 09	2 91	4 22	1 451	0 649
Polymer M	0 5	95 27%	3 32	2 91	4 33	1 487	0 662
Polymer M	0 75	95 80%	3 22	2 74	4 18	1 523	0 649
Polymer M	1	96 23%	3 38	2 71	4 29	1 583	0 651
Bentonite Clay	2	89 95%	3 32	3 25	4 51	1 391	0 724
Bentonite Clay	4	93 96%	3 11	3 08	4 38	1 420	0 678
Bentonite Clay	6	96 47%	4 61	2 96	4 21	1 423	0 649

[0209] Another series of Britt jar retention and CSF drainage tests is conducted with Polymer III and Polyflex CP.3, that utilizes higher levels of CPAM-P flocculant and an additional flocculant, polyvinylamine (PVAm). The PVAm is produced via aqueous solution polymerization of N-vinylformamide monomer, then with a subsequent hydrolysis of the polymer to produce N-vinylamine. The subject polymer is hydrolyzed at 90%, such that the resultant copolymer is 90 mole % N-vinylamine/10 mole % N-vinylformamide; the polymer is at 5% solids and exhibits an intrinsic viscosity in 1 M NaCl of 3 dL/g. The data in Table 10 demonstrates the utility of the HAP at higher levels of CPAM-P flocculant, and activity with a PVAm flocculant.

TABLE 10

Add #1	lbs/ton (active)	Add #2	lbs/ton (active)	Add #3	lbs/ton (active)	Drainage Aid	lbs/ton (active)	Avg Ret	CSF
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	none	0	53.6	370
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polyflex CP 3	0.75	78.6	650
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	0.5	Polymer III	0.75	70.8	595
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	1	none	0	66.6	395
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	1	Polyflex CP 3	0.75	91.6	680
Cationic Potato Starch	10	Alum	5	CPAM-P Flocculant	1	Polymer III	0.75	80.9	610
Cationic Potato Starch	10	Alum	5	PV Am Flocculant	0.5	none	0	35.9	435
Cationic Potato Starch	10	Alum	5	PV Am Flocculant	0.5	Polyflex CP.3	0.75	91.1	730
Cationic Potato Starch	10	Alum	5	PV Am Flocculant	0.5	Polymer III	0.75	74.0	665

[0210] Another series of PDD experiments is conducted as presented in Table 11 under the procedures described previously, with Polymer III, Polyflex CP.3, and two additional Polyflex products, Polyflex CS and Polyflex CP.2, also available from Cytec Industries, Inc. The data in Table 11 demonstrates that the inventive Polymer III provides improved retention and drainage activity compared to Polyflex CP.2, equivalent activity as Polyflex CS, and activity approaching Polyflex CP.3.

TABLE 11

10 Lbs./Ton Cationic Potato Starch + 5 Lbs./Ton 0.5 Lbs./Ton CPAM-P Flocculant + Drainage Aid	lbs/ton (Active)	% First Pass Fines Retention	Gravity Drainage Time - seconds	VACUUM Equilibrium (in Hg)	PEAK VACUUM (in Hg)	Peak to Equilibrium Vacuum Ratio	Vacuum Drainage Time - seconds
None	0	85.2%	3.44	3.61	5.41	1.50	1.15
Polyflex CP 3	0.5	92.6%	3.12	2.77	4.28	1.55	0.64
Polyflex CP 3	0.75	94.1%	3.09	2.52	3.97	1.58	0.55
Polymer CP 3	1	93.5%	3.00	2.44	3.79	1.55	0.54
Polyflex CS	0.5	91.6%	3.12	3.20	4.75	1.48	0.75
Polyflex CS	0.75	92.8%	3.13	3.07	4.61	1.50	0.72
Polyflex CS	1	95.9%	3.20	2.92	4.47	1.53	0.67
Polyflex CP 2	0.5	91.6%	3.16	3.33	4.78	1.43	0.75
Polyflex CP 2	0.75	92.7%	3.16	3.27	4.73	1.45	0.77
Polyflex CP 2	1	91.2%	3.27	3.39	4.75	1.40	0.75
Polymer III	0.5	89.5%	3.35	3.30	4.77	1.44	0.80
Polymer III	0.75	94.0%	3.11	3.07	4.64	1.51	0.73
Polymer III	1.00	94.3%	3.13	3.01	4.57	1.52	0.68
Polymer E	0.5	91.9%	3.14	2.97	4.60	1.55	0.70
Polymer E	0.75	95.4%	3.08	2.75	4.54	1.65	0.70
Polymer E	1	92.9%	3.20	2.66	4.60	1.73	0.75

[0211] A series of Britt jar retention and CSF drainage studies is conducted with the brine dispersion polymers described previously. These studies set forth in Table 12 are conducted with Polymers IX and X, polymers of the inventive method modified with lauryl methacrylate; Polymers XI and XII, polymers of the inventive method modified with lauryl acrylate; Polymer VIII is the control polymer, produced under equivalent conditions as the hydrophobically associated polymers, but does not contain the hydrophobic substitution; Polyflex CP.3, and Polymer A, a conventional high MW anionic polyacrylamide powder flocculant. The test conditions and associated additives are as those described before, with the exception of the cationic flocculant utilized being CPAM-N; this material is equivalent in composition and physical form as the previously utilized CPAM-P. An anionic polyacrylamide flocculant (APAM) is also utilized. This material is a 30 mole % sodium acrylate/70 mole % acrylamide copolymer, commercially available as a self-inverting emulsion. The data in Table 12 demonstrates the improved activity of the inventive material. Polymers IX and XI demonstrate high retention and drainage activity compared to commercial drainage aid bentonite clay, the control Polymer VIII, and the conventional flocculant Polymer A. This improved activity is observed when utilized with a CPAM flocculant, with an APAM flocculant, and without a flocculant.

TABLE 12

Add #1	lbs/ton (active)	Add #2	lbs/ton (active)	Add #3	lbs/ton (active)	Drainage Aid	lbs/ton (active)	Avg Ret	CSF Drainage
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	None	0	53.6	370
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer VIII	0.75	71.1	620
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer IX	0.75	78.9	650
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer XI	0.75	76.4	640
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer X	0.75	73.1	630
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer XII	0.75		555
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polyflex CP 3	0.75	86.0	680
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Polymer A	0.75	68.1	620
Cationic Potato Starch	10	Alum	5	CPAM-N Flocculant	0.5	Bentolite HS	4	70.7	630
Cationic Potato Starch	10	Alum	5	None	0	Polymer VIII	0.5	59.6	560
Cationic Potato Starch	10	Alum	5	None	0	Polymer IX	0.5	66.0	545
Cationic Potato Starch	10	Alum	5	None	0	Polymer XI	0.5	67.8	555
Cationic Potato Starch	10	Alum	5	None	0	Polymer X	0.5	52.0	495
Cationic Potato Starch	10	Alum	5	None	0	Polymer XII	0.5		435

TABLE 12-continued

Add #1	lbs/ton (active)	Add #2	lbs/ton (active)	Add #3	lbs/ton (active)	Drainage Aid	lbs/ton (active)	Avg Ret	CSF Drainage
Cationic Potato Starch	10	Alum	5	None	0	Polyflex CP 3	0.5	71.5	585
Cationic Potato Starch	10	Alum	5	None	0	Polymer A	0.5	57.1	560
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer VIII	0.5		530
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer IX	0.5		565
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer XI	0.5		540
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer X	0.5		540
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer XII	0.5		520
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polyflex CP 3	0.5		630
Cationic Potato Starch	10	Alum	5	APAM Flocculant	0.5	Polymer A	0.5		505

[0212] A series of evaluations is conducted on the PDD, utilizing equivalent methods as described in Table 12. The studies set forth in Table 13 are conducted with Polymers IX and X, polymers of the inventive method modified with lauryl methacrylate; Polymers XI and XII, polymers of the inventive method modified with lauryl acrylate; Polymer VII is the control polymer, produced under equivalent conditions as the hydrophobically associated polymers, but does not contain the hydrophobic substitution; and Polyflex CP.3. The data in Table 13 demonstrates positive drainage activity for Polymers IX, X, and XI compared to the unmodified control Polymer VIII. The Polymers IX, X, and XI also indicate a positive dosage response at low PEVR, while the unmodified control does not demonstrate a remarkable dosage response.

TABLE 13

10 lbs/ton Cat Potato Starch + 5 lbs/ton 0.5 lbs/ton CPAM-N Flocculant + Drainage Aid	lbs/ton (Active)	% First Pass Fines Retention	Gravity Drainage Time - seconds	VACUUM Equilibrium (in Hg)	PEAK VACUUM (in Hg)	Peak to Equilibrium Vacuum Ratio	Vacuum Drainage Time- seconds
None		86.1%	3.98	3.33	5.11	1.53	0.94
Polymer VIII	0.5	93.1%	3.76	2.89	4.38	1.52	0.67
Polymer VIII	1	95.6%	3.79	2.72	4.18	1.54	0.63
Polymer IX	0.5	93.7%	3.71	2.77	4.12	1.49	0.64
Polymer IX	1	94.5%	3.64	2.51	3.75	1.50	0.54
Polymer X	0.5	92.5%	3.69	2.79	4.12	1.48	0.65
Polymer X	1	97.2%	3.66	2.48	3.72	1.50	0.55
Polymer XI	0.5	94.0%	3.65	2.74	4.07	1.49	0.62
Polymer XI	1	93.7%	3.68	2.49	3.87	1.55	0.54
Polymer XII	0.5	86.0%	3.86	3.23	4.69	1.45	0.77
Polymer XII	1	89.1%	3.73	3.00	4.43	1.47	0.71
Polyflex CP 3	0.5	95.8%	3.70	2.60	3.93	1.51	0.57
Polyflex CP.3	1	94.9%	3.55	2.29	3.52	1.54	0.49

[0213] 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 which 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; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

1. A method of making a cellulosic fiber composition which comprises adding, to a cellulosic pulp slurry, a hydrophobically associative polymer comprised of recurring units of at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent, and recurring units of at least one monomer selected from a nonionic ethylenically unsaturated monomer, a cationic ethylenically unsaturated monomer, or an anionic ethylenically unsaturated monomer, with the proviso that the at least one hydrophobic ethylenically unsaturated monomer does not contain 2,4,6-triphenylethyl benzene.

2. The method of claim 1 wherein the hydrophobic ethylenically unsaturated monomer comprises an ethylenically unsaturated monomer having at least one pendant hydrophobic group.

3. The method of claim 2 wherein the pendant hydrophobic group is selected from one or more of C₄ to C₂₀ alkyls, C₄ to C₂₀ cycloalkyls, polynuclear aromatic hydrocarbon groups, alkaryls wherein alkyl has one or more carbons; haloalkyls of four or more carbons, or polyalkyleneoxy groups.

4. The method of claim 3 wherein the hydrophobic group is selected from one or more of C₄-C₂₀ alkyl groups.

5. The method of claim 3 wherein the hydrophobic group is selected from one or more of C₈-C₂₀ alkyl groups.

6. The method of claim 1 wherein the hydrophobic ethylenically unsaturated monomer is selected from one or more hydrocarbon esters of ethylenically unsaturated carboxylic acids and their salts.

7. The method of claim 1 wherein the hydrophobic ethylenically unsaturated monomer is selected from one or more of the C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid.

8. The method of claim 1 wherein the nonionic ethylenically unsaturated monomer is selected from one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone.

9. The method of claim 8 wherein the N-alkylacrylamide is N-methylacrylamide.

10. The method of making the cellulosic fiber composition of claim 8 wherein the at least one nonionic ethylenically unsaturated monomer is selected from one or more of acrylamide, methacrylamide, or N-alkylacrylamides.

11. The method of making the cellulosic fiber composition of claim 8 wherein the at least one nonionic ethylenically unsaturated monomer is acrylamide.

12. The method of making the cellulosic fiber composition of claim 1 wherein the at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl-(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof.

13. The method of making the cellulosic fiber composition of claim 12 wherein the at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid or the salts thereof.

14. The method of making the cellulosic fiber composition of claim 13 wherein the at least one anionic ethylenically unsaturated monomer is selected from one or more of the sodium or ammonium salts of acrylic acid.

15. The method of making the cellulosic fiber composition of claim 1 wherein the at least one hydrophobic ethylenically unsaturated monomer groups is present in an amount from about 0.01 mole percent to about 1 mole percent.

16. A method of making a cellulosic fiber composition which comprises adding, to a cellulosic pulp slurry, a water soluble hydrophobically associative polymer comprising:

recurring units of at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent and selected from one or more of C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid;

recurring units of at least one nonionic ethylenically unsaturated monomer is selected from one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone;

recurring units of at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonate, sulfoethyl-(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof.

17. The method of making a cellulosic fiber composition of claim 16 wherein the water soluble hydrophobically associative polymer comprises:

recurring units of at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent and selected from one or more of C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid;

recurring units of at least one nonionic ethylenically unsaturated monomer selected from one or more of acrylamide, methacrylamide, or N-alkylacrylamides;

recurring units of at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid or the salts thereof.

18. A method of making a cellulosic fiber composition which comprises adding, to a cellulosic pulp slurry, a water soluble hydrophobically associative anionic polymer comprising at least one hydrophobic ethylenically unsaturated

monomer selected from one or more of lauryl acrylate or lauryl methacrylate, acrylamide, and acrylic acid.

19. The method of claim 18 wherein the hydrophobic ethylenically unsaturated monomer is lauryl acrylate.

20. The method of claim 18 wherein the hydrophobic ethylenically unsaturated monomer is lauryl methacrylate.

21. A cellulosic fiber composition comprising an aqueous slurry of cellulosic pulp and a water soluble hydrophobically associative polymer, wherein the polymer comprises:

recurring units of at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent, and

recurring units of at least one monomer selected from a nonionic ethylenically unsaturated monomer, a cationic ethylenically unsaturated monomer, or an anionic ethylenically unsaturated monomer,

with the proviso that the at least one hydrophobic ethylenically unsaturated monomer does not contain 2,4,6-triphenoethyl benzene.

22. The cellulosic fiber composition of claim 21 wherein the at least one hydrophobic ethylenically unsaturated monomer comprises an ethylenically unsaturated monomer having at least one pendant hydrophobic group.

23. The cellulosic fiber composition of claim 22 wherein the pendant hydrophobic group is selected from one or more of C₄ to C₂₀ alkyls, C₄ to C₂₀ cycloalkyls, polynuclear aromatic hydrocarbon groups, alkaryls wherein alkyl has one or more carbons; haloalkyls of four or more carbons, or polyalkyleneoxy groups.

24. The cellulosic fiber composition of claim 23 wherein the at least one hydrophobic group is selected from one or more of C₄-C₂₀ alkyl groups.

25. The cellulosic fiber composition of claim 24 wherein the at least one hydrophobic group is selected from one or more of C₈-C₂₀ alkyl groups.

26. The cellulosic fiber composition of claim 21 wherein the at least one hydrophobic ethylenically unsaturated monomer is selected from one or more hydrocarbon esters of ethylenically unsaturated carboxylic acids and their salts.

27. The cellulosic fiber composition of claim 26 wherein the at least one hydrophobic ethylenically unsaturated monomer is selected from one or more of the C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid.

28. The cellulosic fiber composition of claim 21 wherein the at least one nonionic ethylenically unsaturated monomer is selected from one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone.

29. The cellulosic fiber composition of claim 28 wherein the at least one nonionic ethylenically unsaturated monomer is acrylamide.

30. The cellulosic fiber composition of claim 21 wherein the at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl-

(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof.

31. The cellulosic fiber composition of claim 30 wherein the at least one anionic ethylenically unsaturated monomer is selected from one or more of the sodium or ammonium salts of acrylic acid.

32. The cellulosic fiber composition of claim 21 wherein the at least one hydrophobic ethylenically unsaturated monomer groups is present in an amount from about 0.01 mole percent to about 1 mole percent.

33. A cellulosic fiber composition comprising an aqueous slurry of cellulosic pulp and a water soluble hydrophobically associative polymer wherein the polymer comprises:

recurring units of at least one hydrophobic ethylenically unsaturated monomer present in an amount from about 0.001 mole percent to about 10 mole percent and selected from one or more of C₁₀-C₂₀ alkyl esters of acrylic and methacrylic acid;

recurring units of at least one nonionic ethylenically unsaturated monomer is selected from one or more of acrylamide, methacrylamide, N-alkylacrylamides, N,N-dialkylacrylamides, methyl acrylate, methyl methacrylate, acrylonitrile, N-vinyl methylacetamide, N-vinyl methyl formamide, vinyl acetate, or N-vinyl pyrrolidone; recurring units of at least one anionic ethylenically unsaturated monomer is selected from one or more of acrylic acid, methacrylic acid, 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl-(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic acid or the salts thereof.

34. The cellulosic fiber composition of claim 33 wherein the water soluble hydrophobically associative polymer comprises:

at least one hydrophobic ethylenically unsaturated monomer selected from one or more of dodecyl acrylate or dodecyl methacrylate,

the at least one nonionic ethylenically unsaturated monomer is acrylamide,

the at least one anionic ethylenically unsaturated monomer is selected from one or more of the sodium or ammonium salts of acrylic acid.

35. The cellulosic sheet of claim 33 comprising paper.

36. A cellulosic fiber composition comprising an aqueous slurry of cellulosic pulp and a water soluble hydrophobically associative polymer wherein the polymer comprises:

recurring units of a hydrophobic ethylenically unsaturated monomer selected from one or more of lauryl acrylate or lauryl methacrylate,

recurring units of a nonionic ethylenically unsaturated monomer is acrylamide, and

recurring units of an anionic ethylenically unsaturated monomer is acrylic acid.

37. The cellulosic sheet of claim 36 comprising paper.

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