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(54) USE OF VINYLAMINE POLYMERS WITH IONIC, ORGANIC, CROSS-LINKED POLYMERIC MICROBEADS IN PAPER-MAKING

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(57) ABSTRACT

A method for making paper is disclosed. The method comprising adding to a furnish comprising cellulosic, paper-making fibers (i) from about 0.05 to about 20 pounds per ton, based upon the dry weight of the furnish solids, of an ionic, organic, crosslinked polymeric microbead with a diameter of less than about 500 nm, and (ii) from about 0.05 to about 20 pounds per ton, same basis, of a polymeric material, containing vinylamine recurring units. In addition to the compositions described above, additives such as organic ionic, polysaccharides (e.g., a starch), may also be combined with the liquid system to facilitate drainage and retention.

USE OF VINYLAMINE POLYMERS WITH IONIC, ORGANIC, CROSS-LINKED POLYMERIC MICROBEADS IN PAPER-MAKING

TECHNICAL FIELD

[0001] The present invention relates generally to compositions and methods for providing improved liquid-solid separation performance in papermaking processes. More particularly the invention relates to the addition of vinylamine polymers and ionically charged organic polymer microbeads to papermaking systems comprising liquid dispersions of cellulosic fibers for improving drainage, retention and formation in such systems.

BACKGROUND OF THE INVENTION

[0002] Papermaking processes require treatment of a system comprising a liquid dispersion of solid particles for separating the solids therefrom. Fast drainage and greater retention of fines contribute to lower costs in papermaking and thus improvements in this area are always being sought. Improvements in formation are likewise desired as-such improvements result in a better product. One method for improving these properties, which was first practiced during the 1980's, involves the use of colloidal silica and bentonite. The improved drainage offered with the use of these materials, i.e., as indicated by increasing speed and efficiency with greater retention of fines, provides significant cost savings over the prior art techniques.

[0003] U.S. Pat. Nos. 4,385,165 and 4,388,150 describe a two-component binder system comprising a cationic starch and an anionic, colloidal silicic acid sol which acts as a retention aid when combined with cellulose fibers in a paper-making stock. Finnish published specification Nos. 67,735 and 67,736 disclose cationic polymer retention agent compounds comprising cationic starch and polyacrylamide. These materials are described by the subject references as being useful when combined with an anionic silica in improving sizing.

[0004] U.S. Pat. No. 4,798,653 discloses the use of cationic colloidal silica sol in combination with an anionic copolymer of acrylic acid and acrylamide for rendering paper stock resistant to loss of its retention and dewatering properties due to shear forces attributable to the papermaking process.

[0005] A coacervate binder, three-component system composed of a cationic starch, an anionic, high molecular weight polymer and dispersed silica having a particle diameter range from 1 to 50 nm is described in U.S. Pat. Nos. 4,643,801 and 4,750,974.

[0006] The two Finnish patent publications noted above additionally describe the use of bentonite with cationic starch and polyacrylamides) ("PAM(s)") and U.S. Pat. No. 4,305,781 discloses a bentonite-type clay used in combination with high-molecular weight, substantially non-ionic polymers such as polyethylene oxides and PAMs for use as retention agents. U.S. Pat. No. 4,753,710 discloses the use of bentonite with a substantially linear, cationic polymer, e.g., cationic acrylic polymers, polyethylene imine, polyamine epichlorohydrin and dialkyl dimethyl ammonium chloride as providing an improved combination of retention, drainage, drying and formation.

[0007] Another material which has been found useful in separating particulate dispersions of the type contemplated herein is organic crosslinked microbeads. Such microbeads are known to be particularly useful for flocculating a wide variety of dispersions of suspended solids as described, for example, in U.S. Pat. No. 5,171,808, to Ryles et al.

[0008] The use of such organic crosslinked microbeads in papermaking-is taught, e.g., in U.S. Pat. No. 5,180,473. The '473 reference discloses a dual system comprising a cationic organic microbead of 1-100 microns together with an anionic, cationic or nonionic acrylamide polymer. The cationic polymer particle is of the water swelling type and is a crosslinked homopolymer of 2-methacryloyloxyethyl trimethylammonium chloride or a crosslinked copolymer of 2-methacryloxy-ethyl trimethylammonium chloride/acrylamide (60/40 weight percent). The acrylamide polymer is an acrylamide homopolymer or acrylamide hydrolysate of 17 mole percent anion-conversion or a copolymer of acrylamide/2-methacryloyloxyethyltrimethyl ammonium chloride (75/25 weight percent). Japanese Patent Publication No. JP 235596/63:1988, which corresponds to the U.S. '473 patent, discloses the use of both cationic and anionic microbeads. The anionic microbead disclosed by the Japanese reference is an acrylamide-acrylic acid copolymer.

[0009] European Patent No. 0 202 780 describes the preparation of cross-linked cationic polyacrylamide beads by conventional inverse emulsion polymerization techniques. During formation of the beads, the PAM is crosslinked by incorporating a difunctional monomer, such as methylene bis-acrylamide, in a manner well known in the art into the polymer chain. The reference further discloses that the cross-linked beads, while useful as flocculants, are more highly efficient after having been subjected to unusual levels of shearing action in order to render them water soluble.

[0010] Typically, the particle size of polymers prepared by conventional, inverse, water-,in-oil emulsion polymerization processes is limited to the 1-5 micron range since there is no particular advantage known to reduce this particle size. The particle size achievable in inverse emulsions is determinable by the concentration and activity of the surfactants employed, which surfactants are customarily chosen based on the desired emulsion stability as well as on economic factors.

[0011] U.S. Pat. No. 5,167,766 to Honig, et al discloses the addition, in a papermaking process, of ionic, organic microbeads of up to about 750 nm in diameter to obtain improved drainage, retention and formation. These microbeads may be made as microemulsions, as microgels, or as microlatices. The microbeads may be added either alone or in combination with a high molecular weight polymer and/or a polysaccharide as taught in U.S. Pat. No. 5,274,055 to Honig et al. Other standard paper-making additives, including alum or any other active, soluble aluminum species, also may be added for their well known purposes.

[0012] Copending application Ser. No. 08/092,859 filed Jul. 19, 1993 teaches the use of organic, cross-linked, ionic polymeric microbeads and ethylene imine, modified polyethylenimines and mixtures thereof also in paper-making procedures.

[0013] In view of the importance to the papermaking industry, of improving drainage, retention and formation during the production of paper, those working in this field are constantly on the lookout for compositions and methods which are particularly efficient in improving these properties.

SUMMARY OF THE INVENTION

[0014] The present invention is therefore particularly directed to a method useful in providing improved liquid-solid separation performance in papermaking systems comprising dispersions of cellulosic fibers within an aqueous liquid furnish as evidenced by improvements in drainage, formation and retention parameters within such systems. The invention is also useful in a wide variety of other liquid-solid separation processes involving liquid dispersion systems, such systems comprising liquid systems containing finely divided solid particles, which particles, upon treatment in accordance with the method of the invention, are agglomerated for removal from the liquid system. An example of such a system, i.e., in a field other than papermaking, is the treatment of waste water streams wherein the compositions may be added to assist in flocculating, and therefore removing, solids therefrom. A variety of additional examples of such systems are well known in the art. However, for purposes of convenience, the invention is described herein particularly with reference to its use in a papermaking process.

[0015] Accordingly, therefore, in the formation of paper from an aqueous suspension of cellulosic papermaking fibers, the improvements described herein are achieved by the addition to the suspension of: (1) crosslinked, ionic, polymeric microbeads of less than about 500 nm in diameter and (2) a vinylamine polymer.

[0016] The vinylamine polymers useful in the process of the present invention are well known to those skilled in the art and are taught as flocculants and as additives to the furnish of the paper-making process. U.S. Pat. No. 4,217,214, for example, discloses the use of high molecular weight polyvinylamine hydrochloride as a flocculating agent in waste water system for potable water purification and sewage pollution control.

[0017] U.S. Pat. No. 4,421,602 teaches the use of linear, basic copolymers of from 90 to 10 mole percent of copolymerized vinylamine units and 10-90 mole percent of vinyl formamide units as retention agents, drainage assistants and flocculants in paper-making. These copolymers are made by polymerizing N-vinylformamide in the presence of a free radical polymerization initiator and splitting off the formyl group from the resulting polymer at 20°-200° C. in the presence of an acid or base.

[0018] European Published Document 249,891B teaches a process for producing paper, paperboard, and cardboard by draining the pulp slurry in the presence of a high molecular weight, water-soluble, N-vinyl formamide polymer and a synthetic phenol resin or phenol containing natural oligimer or polymer.

[0019] U.S. Pat. No. 4,808,683 teaches the use of vinylamine terpolymers of quaterized vinylamine, i.e. where the amine is converted to, $—{}^{+}NH_3X^{-}$ groups (where X represents an anion or hydroxyl ion), vinylformamide and an N-substituted (meth) acrylamide as flocculating agents, drainage aids and paper strength increasing agents.

[0020] Another patent which teaches the use of vinylamine polymers in paper-making is U.S. Pat. No. 4,818,341 wherein a mixture of water-soluble natural potato starch and a cationic polymer of copolymerized units of diallyldimethylammonium chloride and N-vinylamine or substituted or unsubstituted N-vinylimidazoline is used for dewatering the paper stock.

[0021] High molecular weight poly(N-vinylamides) and hydrolyzed derivatives thereof are taught in U.S. Pat. No. 4,843,118., They are prepared by inverse emulsion polymerization of the N-vinylamide monomer and may thereafter be hydrolyzed with a mineral acid e.g. hydrochloric acid to 10-90% vinylamine groups. Polymers having molecular weights of 1.8×10^6 to 9×10^6 are recovered. Other methods of preparing hydrolyzed vinyl formamide polymers are taught in U.S. Pat. No. 5,324,792, Japanese Patent No. 93056763; U.S. Pat. No. 5,155,167; U.S. Pat. No. 5,290,880 and Japanese Patent No. 93056767.

[0022] Vinylamine polymers similar to those of the above '683 patent but containing, in addition, recurring acrylamide and acrylate groups, and a method for their production are disclosed in U.S. Pat. Nos. 4,957,977 and 5,064,909. Again, the polymers are taught as paper strength increasing agents and flocculating agents.

[0023] Water-soluble copolymers containing copolymerized vinylamine units prepared by copolymerizing 10-95 mole percent of N-vinylformamide and 5-90 mole percent of vinylfacetate, vinyl proprionate, C_1-C_4 alkyl vinyl ethers, the esters, nitriles and amines of (meth)-acrylic acid, N-vinyl carbamate or N-vinyl pyrrolidone are taught in U.S. Pat. No. 4,978,427; DE 4241117-A1 and Japanese 94076462-B2 and 94065366-B2 as dry and wet strength agents and additives for paper and in U.S. Pat. No. 3,715,336 as flocculants.

[0024] In U.S. Pat. Nos. 5,098,521 and 4,774,285, paper, board and cardboard are produced from paper stock using vinylamine/vinylformamide copolymers of certain K values where the vinylamine content is varied. The copolymers are taught as increasing wet and dry strength and as drainage aids while in U.S. Pat. No. 5,324,787 vinylamine polymers which are reacted with aromatic glycidyl ethers are shown to be useful as retention aids.

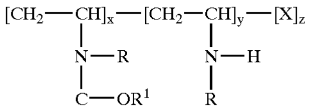
[0025] The use of a fixing agent comprising a hydrolyzed (not less than 60%) homopolymer or copolymer of N-vinylformamide in the presence of a polymeric cationic retention aid in the making of paper, board or cardboard is the subject of U.S. Pat. No. 5,145,559. The retention aids are not, however, in the form of cross-linked microbeads. The use of PVA polymers in conjunction with cross-linking agents such as glyoxal is taught in U.S. Pat. No. 5,281,307.

[0026] Polyvinylaminal polymers containing 1-60 percent of aldehyde induced groups and which are useful as a retention agent in papermaking are taught in U.S. Pat. No. 5,232,553 whereas quaternized polyvinylamine is disclosed in U.S. Pat. No. 5,269,942 for use in the deinking loop of a paper recycling operation and in Canadian Application 2,110,366-A1 as a retention aid, as well as in U.S. Pat. No. 5,281,340.

[0027] Other patents which teach methods of preparing polyvinylamine(s) compositions and their use in papermaking include EP 617,166-A1; EP 617,054-A2; EP 295,615-A1; EP 264,649-A1; EP 331,047-A1; U.S. Pat. No.

5,194,492; Japanese 05255565-A; U.S. Pat. No. 5,292,821; U.S. Pat. No. 5,239,014; U.S. Pat. No. 5,039,757 and EP 489,930-A1. Any and all of the above-referenced vinylamine based polymers maybe used in the process of the present invention and, accordingly, each of said patents is hereby expressly incorporated herein by reference.

[0028] Accordingly, a polymeric material, or salt or quaternary thereof, having recurring units of the formula



$$[CH_2-\underset{\substack{|\\ N-R\\ |\\ C-OR^1}}{CH}]_x-[CH_2-\underset{\substack{|\\ N-H\\ |\\ R}}{CH}]_y-[X]_z$$

[0029] wherein each R or R^1, individually, is hydrogen or a C_1-C_3 alkyl group, X is the polymerization residue of a copolymerizable monmer or hydrolyzed derivative thereof or mixtures of said monomers, x and z are, individually, numerals ranging from about 0 to 99 and y is a numeral ranging from about 1 to about 100, may be used in the instant process.

[0030] Preferably x and z are, individually, numerals ranging from about 0 to about 95, and, most preferably, from about 0 to about 75. Correspondingly, y preferably ranges from about 0.5 to about 100, most perferably from about 25 to about 100.

[0031] Examples of suitable copolymerizable comonomers whose polymerization residue is represented by X in the above formula include, N-methyl(meth) acrylamide, N-ethyl(meth) acrylamide, N'N-dimethyl(meth) acrylamide, N-isopropyl(meth) acrylamide, N-t-butyl(meth) acrylamide, N-(1,1-dimethyl-3-oxobutyl)(meth) acrylamide, diallyldimethylammonium chloride, N-vinylimidazoline, (meth) acrylamide, (meth) acrylonitrile, vinyl acetate, N-vinylpyrrolidone, vinyl urea, C_1-C_4 alkylvinylethers, vinyl propionate, the esters of (meth) acrylic acid and the like.

[0032] The vinylamide monomers useful in producing the x and y recurring units of the above formula include N-vinylformamide, N-vinylacetamide, N-ethyl-N-vinylformamide, N-ethyl-N-vinylacetamide, N-methyl-N-vinylformamide, N-methyl-N-vinylacetamide, N-vinylpropionamide and the like.

[0033] The salts of the polymers can be prepared as taught by the '214 patent to Dubin, above, i.e. by reaction of the amide with an appropriate mineral acid, such as hydrochloric acid, bromic acid, hydrofluoric acid, sulfuric acid, nitric acid, phosphoric acid, sulfamic acid, alkane-sulforic acid and the like.

[0034] Quaternaries of the polymers can be prepared by the method taught by the above-mentioned '942 patent to Harrington et al i.e. by reacting a vinylamine hydrochloride polymer with a quaternizing agent such as methyl chloride, dimethyl sulfate, benzene chloride etc. followed by concentration and dialysis to remove salts.

[0035] Hydrolysis of the X monomer residue units may be conducted in the manner taught by the '683 patent to Itagaki et al discussed above i.e. acid hydrolysis in water, acid hydrolysis in a hydrophilic solvent such as alcohol, containing water, etc.

[0036] Preferably, in the above formula, R is hydrogen and y is 100.

[0037] The weight average molecular weight of the vinylamine polymers useful in the present invention may range from about 3000 to about 10 million preferably about 50,000 to about 5 million.

[0038] In preparing the microbeads for use in the process of the present invention, crosslinked, organic polymeric microbeads having a particle size less than about 500 nm in diameter and preferably less than about 300 nm in diameter, with the most preferred diameter being between about 25-300 nm, are used. The addition of such microbeads in combination with the vinylamine polymers, provides substantial improvements in e.g., drainage time, in systems in which the subject materials have been added.

[0039] One embodiment of the present invention comprises adding to a particulate paper-making suspension, e.g., of cellulosic papermaking fibers, from about 0.05 to 20 pounds per ton of organic microbeads, i.e., of a diameter as described above, preferably about 0.1 to about 10 pounds and from about 0.05 to about 20 pounds per ton, preferably about 0.1 to 10 pounds per ton, of the vinylamine polymer. The pounds/ton of the materials used is based on the dry weight of the solids in solution. The ratio of the microbeads to the vinylamine polymer should range from about 1:10 to about 10:1,preferably, from about 1:4 to about 4:1, respectively. The vinylamine polymers and microbead used in the process of the present invention have been found to be particularly effective when used to treat slurries of papermaking fibers wherein the percent solids in the furnish is over about 0.2.

[0040] Additionally, best results are achieved when the furnish has a pH of about 7.0 or higher, preferably about 8.0. In a preferred embodiment, the furnish is an alkaline, calcium carbonate or calcium sulfate filled paper-making stock.

[0041] The microbeads used in the method of the invention may be made as microemulsions by a process employing an aqueous solution comprising an ionic, preferably an anionic, monomer and a crosslinking agent; an oil comprising a saturated, hydrocarbon and an effective amount of a surfactant sufficient to produce particles of less than about 0.5 micron in particle size diameter. Polymerization of the emulsion may be accomplished by the addition of a polymerization initiator, or by subjecting the emulsion to ultraviolet radiation. In addition, an effective amount of a chain transfer agent may be added to the aqueous solution of the emulsion to control the polymerization.

[0042] The microbeads may also be made as microgels by procedures described by Huang et al., *Macromolecular Chemistry* 186', 273-281 (1985); Fukatomi et al., *J. Appl. Polymer Sci.* 44, 737-741 (1992) and Kawaguchi et al., *Polymer Int'l.* 30, 225-231 (1993), or they may be obtained commercially as microlatices.: The term "microbead" as used-herein includes all of these configurations, i.e., beads, microgels and mictolatices.

[0043] In a preferred embodiment of the invention, anionic microbeads are added with cationic vinylamine polymer. Alternatively, however, the invention also contemplates the addition of cationic beads with the vinylamine polymer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0044] As noted above, addition of the materials described herein, namely: (1) ionic, organic, crosslinked polymeric microbeads having a diameter of less than about 500 nm and (2) a vinylamine polymer, to a liquid dispersion: of cellulosic fibers within a papermaking system according to the invention will result in improved drainage and formation as well as greater fines and, filler retention values. Moreover, as also noted, these materials are additionally useful in a variety of other liquid-solid separation techniques, such as in the removal by flocculation of particulates from waste water streams e.g. sludge dewatering.

[0045] In one embodiment of the invention, only the microbeads and the vinylamine polymer are added to the dispersion, while in an alternate embodiment the vinylamine polymer and microbeads are added in conjunction with one or more additives (as discussed below), to a conventional acid, neutral or, alkaline papermaking stock such as traditional chemical pulps, e.g., bleached and unbleached sulphate or sulphite pulp, mechanical pulp such as groundwood, thermomechanical or chemi-thermomechanical pulp or recycled pulp such as old corrugated containers, newsprint, office waste, magazine paper and other non-deinked waste, deinked waste and mixtures thereof. The stock and final paper can be substantially unfilled or filled with amounts of up to 50%, based upon the dry weight of the stock, or up to about 40%, based upon the dry weight of paper in the filler, being exemplary.

[0046] When a filler is used, any conventional filler, such as calcium carbonate, clay, titanium dioxide, talc, or a combination thereof may be present: The filler, if present, may be incorporated into the stock either before or after the addition of the microbeads and the vinylamine polymer.

[0047] In a most preferred embodiment, the furnish is a neutral of alkaline paper-making stock having, a pH of 7.0 or above.

[0048] Even more preferred, is an alkaline, paper-making stock having a pH of above 7.0 and containing calcium carbonate or calcium sulfate as a filler.

[0049] As noted above, a wide variety of standard papermaking additives may also be added to the dispersion for their usual purposes. These additives include rosin sizing, synthetic sizings such as alkyl succinic anhydride and alkyl ketene, dimer, alum or any other active soluble aluminum species such as polyhydroxy aluminum chloride and/or sulfate, sodium aluminate and mixtures thereof, strength additives, promoters, polymeric coagulants such as low molecular weight polymers., i.e., having a molecular weight less than or equal to 100,000, dye fixatives, and other materials that are useful in the papermaking process as would be well known in the art. The order of addition, specific addition points, and furnish modification itself are not critical. Rather, these considerations are based upon practicality and performance for each specific application.

[0050] In the process of the invention the preferred sequence of addition is to add the vinylamine polymer first, followed by the microbeads. In a preferred embodiment, the invention utilizes cationic vinylamine polymer and anionic microbeads, although the use of the polymer with cationic microbeads will also provide acceptable results and is considered within the scope of the present invention.

[0051] In a further embodiment of the invention, in addition to the vinylamine polymer and microbeads described above, a third component may be added to the particulate dispersion, namely from about 1 to 50, preferably about 5 to 30, pounds per ton, based on the dry cellulosic fibers, of an organic polysaccharide, such as a starch, said polysaccharide preferably having a charge opposite to that of the microbead. In instances involving the addition of a cationic polysaccharide and cationic vinylamine polymer, these materials can be added separately or together, and in any order. Furthermore, these materials may be individually added at more than one point. The anionic microbeads may be added before any cationic components, or alternately after them, with the latter being the preferred method. If desired, split addition may also be practiced.

[0052] In summary, therefore, the addition points utilized in the method of the invention are those typically used with dual retention and drainage systems (pre-fan pump or pre-screen for one component and pre- or post-screens for another). However, adding the last component before the fan pump may be warranted in some cases. Other addition points that are practical can be used with better performance or convenience often being obtained. Thick stock addition of one component is also possible, although thin stock addition is preferred. Thick stock and/or split thick and thin stock addition of cationic starch are further alternatives. These addition modes are applicable for the microbeads as well. Addition points may be determined by practicality and by the need to place more or less shear on the treated system to ensure good formation.

[0053] The degree of substitution of cationic starches (or other polysaccharides) and other non-synthetic based polymers may be from about 0.01 to about 1.0, preferably from about 0.02 to about 0.2. Amphoteric starches, preferably but not exclusively with a net cationic starch, may also be used. The degree of substitution of anionic starches (or other polysaccharides) and other non-synthetic-based polymers may be from about 0.01 to about 0.7 or greater.

[0054] The ionic starch may be made from starches derived from any of the common starch-producing materials, e.g., potato starch, corn starch, waxy maize, etc. For example, a cationic potato starch may be made by treating potato starch with 3-chloro-2-hydroxypropyl trimethylammonium chloride. Mixtures of synthetic polymers and, e.g., starches, may be used. Other polysaccharides useful herein include guar, cellulose derivatives such as carboxymethylcellulose and the like.

[0055] The preferred vinylamine polymers are polyvinylamine, polyvinylamine hydrochloride and-polyvinylamine formate. These materials are preferred mainly due to the fact that they are more easily prepared.

[0056] The principal advantage observed-by the use of-the process of present invention concerns the fact that the use of the combination of the microbeads (particularly if anionic) and the polyvinylamine polymer results in superior retention, formulation and/or drainage moreover, the combination, when utilized in alkaline paper-making processes, particularly those wherein the furnish contains calcium as a filler, provides even more-spectacular results when compared to existing procedures.

[0057] As a further advantage, the addition of the above-described materials eliminates the need for-alum or other aluminum salts which are sometimes required in prior art systems, thus reducing both the cost and complexity of the paper forming process.

[0058] Turning now to a discussion of the microbeads useful in the invention., these materials are crosslinked, ionic (i.e., cationic or anionic), polymeric organic microparticles having an average particle size diameter of about 500 nm or less, preferably less than about 300 nm and most preferably between about 25-300 nm and a crosslinking agent content of above about 4 molar parts per million, based on the monomeric units present in the polymer. More preferably, a crosslinking content of from-about 4 to about 6,000 molar parts per million is used, most preferably, about-20 to 4,000. The beads are generally formed by the polymerization of at least one ethylenically unsaturated cationic or anionic monomer and, optionally, at least one non-ionic comonomer in the presence of the crosslinking agent. The microbeads preferably have a solution viscosity ("SV") of about 1.1-2 mPa.s. Most preferably, the ionicity is anionic.

[0059] The anionic microbeads preferred for use herein are those made by hydrolyzing acrylamide polymer microbeads, and those made by polymerizing such monomers as (meth)acrylic acid and their salts,

[0060] 2-acrylamido-2-methyl-propane sulfonate, sulfoethyl-(meth)acrylate, vinylsulfonic acid, styrene sulfonic acid, maleic or other dibasic acids or their salts or mixtures thereof.

[0061] Nonionic monomers suitable for making microbeads as copolymers with the above anionic and cationic monomers, or mixtures thereof, include (meth)acrylamide; N-alkylacrylamides such as N-methylacrylamide; N,N-dialkylacrylamides such as N,N-dimethylacrylamide, methyl acrylate; methyl methacrytate; acrylonitrile; N-vinyl-methylacetamide; N-vinyl methyl formamide; vinyl acetate; N-vinyl pyrrolidone, mixtures of any of the foregoing and the like.

[0062] These ethylenically unsaturated, non-ionic monomers may be copolymerized, as mentioned above, to produce cationic, anionic or amphoteric copolymers. Preferably, acrylamide is copolymerized with an anionic and/or a cationic monomer. Cationic or anionic copolymers useful in making the microbeads described herein comprise up to about 99 parts by weight of non-ionic monomer and from about 100 to about 1 part by weight of cationic or anionic monomer, based on the total weight of the anionic or cationic and non-ionic monomers, preferably from about 10 to about 90 parts by weight of non-ionic monomer and about 10 to about 90 parts by, weight of cationic or anionic monomer, same basis, i.e., the total ionic charge in the microbead must be greater than about 1%. Mixtures of polymeric microbeads may also be used if the total ionic charge of the mixture is also over about 1%.

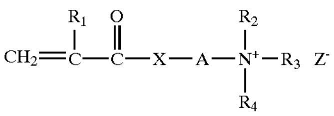
[0063] Most preferably, the microbeads used in the-invention contain from about 20 to 80 parts by weight of non-ionic monomer and about 80 to about 20 parts by weight, same basis, of cationic or anionic monomer or a mixture thereof. Polymerization of the monomers occurs in the presence of a polyfunctional crosslinking agent as noted above to form the crosslinked microbead. Alternatively, the preformed polymer itself may be crosslinked as taught, for example, in U.S. Pat. No. 4,956,400, the disclosure of which is specifically incorporated herein by reference thereto.

[0064] Useful polyfunctional crosslinking agents comprise compounds having either at least two double bounds, a double bond and a reactive group, or two reactive groups. Illustrative of those containing at least two double bounds are N,N-methylenebisacrylamide; N,N-methylenebismethacrylamide; polyethyleneglycol diacrylate; polyethyleneglycol dimethacrylate; N-vinyl acrylamide; divinylbenzene; triallylammonium salts, N-methylallylacrylamide and the like. Polyfunctional branching agents containing at least one double bond and at least one reactive group include glycidyl acrylate; glycidyl methacrylate; acrolein; methylolacrylamide and the like. Polyfunctional branching agents containing at least two reactive groups include dialdehydes, such as, glyoxal; diepoxy compounds; epichlorohydrin and the like.

[0065] The less preferred, but still useful cationic microbeads for use in the invention include those made by polymerizing such monomers as diallyldialkylammonium halides; acryloxyalkyltrimethylammonium chloride; (meth-)acrylates of dialkylaminoalkyl compounds, and salts and quaternaries thereof-and monomers of N,N-diakylaminoalkyl(meth)acrylamides, and salts and quaternaries thereof, such as N,N-dimethyl aminoethyladrylamides; (meth)acrylamidopropyltriethylammonium chloride and the acid or quaternary salts of N,N-dimethylaminoethylacrylate and the like; salts and quaternaries thereof of polyacrylamides formed by chemical reactions on the polyacrylamide (e.g., the Mannich reaction of dimethylamine and formaldehyde on polyacrylamide).

[0066] Cationic monomers which may be used herein are of the following general formulae:

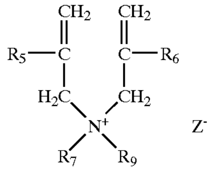
(I)



$$CH_2{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-X-A-\overset{R_2}{\underset{R_4}{N^+}}-R_3\quad Z^-$$

[0067] where R_1 is hydrogen or methyl, R_2 is hydrogen or a lower alkyl of C_1 to C_4, R_3 and/or R_4 are hydrogen, an alkyl of C_1 to C_{12}, aryl, or hydroxyethyl and R_2 and R_3 or R_2 and R_4 can be combined 0.5 to form a cyclic ring containing one or more hetero atoms, Z is the conjugate base of an acid, X is oxygen or —NR_1 wherein R_1 is as defined above, and A is an alkylene group of C_1 to C_{12}, or

(II)



[0068] where R_5 and R_6 are hydrogen or methyl, R_1 is hydrogen, an alkyl of C_1 to C_{12}, or benzyl and R_8 is hydrogen, alkyl of C_1-C_{12}, benzyl or hydroxyethyl; and Z is as defined above.

[0069] The polymeric microbeads of this invention are preferably prepared by polymerization of the monomers in a microemulsion as disclosed in U.S. Pat. No. 5,171,808 to Harris et al., the disclosure of which is expressly incorporated herein by reference thereto. Polymerization in microemulsions and inverse emulsions may also be used as is known to those skilled in this art. P. Speiser reported in 1976 and 1977 a process for making spherical "nanoparticles" with diameters less than 800 Å by: (1) solubilizing monomers, such as acrylamide and methylenebisacrylamide in micelles, and (2) polymerizing the monomers, See *J. Pharm. Sa.,* 65.(12), 1763 (1976) and U.S. Pat. No. 4,021,364. Both inverse water-in-oil and oil-in-water "nanoparticles" were prepared by this process. While not specifically called microemulsion polymerization by the author, this process does contain all the features which are currently used to define microemulsion polymerization. These reports also constitute the first: examples of polymerization of acrylamide in a microemulsion:. Since then, numerous publications reporting polymerization of monomers in microemulsions have appeared. See, for example, U.S. Pat. Nos. 4,521,317 and 4,681,912; Stoffer and Bone, *J. Dispersion Sci. and Tech.,* 1(1), 37, 1980; and Atik and Thomas, *J. Am. Chem. Soc.,* 103 (14), 4279 (1981); and UK patent publication No. GB 2161492A.

[0070] The anionic and/or cationic emulsion polymerization process is conducted by: (i) preparing a monomer emulsion by adding an aqueous solution of the monomers to a hydrocarbon liquid containing an appropriate surfactant or surfactant mixture to form an inverse monomer emulsion consisting of small aqueous droplets which, when polymerized, result in polymer particles less than 0.5 micron in size dispersed in the continuous oil phrase and (ii) subjecting the monomer microemulsion to free radical polymerization.

[0071] The aqueous phase comprises an aqueous mixture of the anionic: and/or cationic monomers and optionally, a non-ionic monomer and the crosslinking agent, as discussed above. The aqueous monomer mixture may also comprise such conventional additives as are desired. For example, the mixture may contain chelating agents to remove polymerization inhibitors, pH adjusters, initiators and other conventional additives.

[0072] Essential to the formation of the emulsion, which may be defined as a swollen, transparent and thermodynamically stable emulsion comprising two liquids insoluble in each other and a surfactant, in which the micelles are less than 0.5 micron in diameter, is the selection of an appropriate organic phrase and a surfactant.

[0073] The selection of the organic phase has a substantial effect on the minimum surfactant concentration necessary to obtain the inverse emulsion. The organic phase may comprise a hydrocarbon or hydrocarbon mixture. Saturated hydrocarbons or, mixtures thereof are the most suitable in order to obtain inexpensive formulations. Typically, the organic phase will comprise benzene, toluene, fuel oil, kerosene, odorless mineral spirits or mixtures of any of the foregoing.

[0074] The ratio, by weight, of the amounts of aqueous and hydrocarbon phases is chosen as high as possible, so as to obtain, after polymerization, an emulsion of high polymer content. Practically, this ratio may range, for example, from about 0.5 to about 3:1, and usually approximates 1:1.

[0075] The one or more surfactants are selected in order to obtain Hydrophilic Lipophilic Balance ("HLB") values ranging: from about 8 to about 11. Outside this range, inverse emulsions are not usually obtained. In addition to the, appropriate HLB value, the-concentration of surfactant must also be optimized, i.e., sufficient to form an inverse emulsion. Too low a concentration of surfactant leads to inverse emulsions as produced in the prior art and too high a concentration results in undue costs. Typical useful surfactants, in addition to those specifically discussed; above, may be anionic, cationic or nonionic surfactants which may be selected from e.g. polyoxyethylene (20) sorbitan trioleate, sorbitan trioleate, sodium di-2-ethylhexylsulfosuccinate, oleamidopropyldimethylamine; sodium isostearyl-2-lactate and the like.

[0076] Polymerization of the emulsion may be carried out in any manner known to those skilled in the art. Initiation may be effected with a variety of thermal and redox free-radical initiators including azo compounds, such as, azobisisobutyronitrile; peroxides, such as t-butyl peroxide; organic compounds, such as potassium persulfate and redox couples, such as ferrous ammonium sulfate/ammonium persulfate. Polymerization may also be effected by photochemical irradiation processes, irradiation, or by ionizing radiation with a ^{60}Co source. Preparation of an aqueous product from the polymer emulsion may be effected by inversion by adding it to water which may contain a surfactant. Optionally, the polymer may be recovered from the emulsion by stripping or by adding the emulsion to a solvent which precipitates the polymer, e.g., isopropanol, filtering off the resultant solids, drying and redispersing in water.

[0077] The following examples are set forth for purposes of illustration only and are not to be construed as limitations on the present invention except as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

[0078] In the examples which follow, the testing simulates adding the ionic polymer microbead after the screen and the vinylamine polymer additive before the screen.

[0079] Drainage is a measure of the time required for a certain volume of water to drain through the paper and is here m measured as a10× drainage (see, e.g., K. Britt, TAPPI 63 (4),) 67 (1980).

[0080] The consistency for the drainage test with alkaline fine paper furnishes is usually adjusted to 0.3-0.4% in order to have reasonablef drainage times. Retention is measured in a Britt Dynamic Drainage Jar. First Pass Retention (FPR) is calculated as follows:

$$FPR = \frac{\text{Headbox Consistency} - \text{Tray Water Consistency}}{\text{Head Box Consistency}}$$

[0081] First Pass Retention is a measure of the percent of solids that are retained in the paper.

[0082] In all examples, the vinylamine polymer and the microbead are added separately to the thin stock and subjected to shear. Except when noted, the charged microbead (or bentonite) is added last. Unless noted, the first of the additives was added to the test furnish in a "Vaned Britt Jar" and subjected to 1500 rpm stirring for 30 seconds for cationics and 800 rpm stirring for 30 seconds for anionics.

[0083] Doses herein are given in pounds/ton for furnish solids such as pulp, fillers etc. Polymers are given on a real-basis and starch, clay and bentonite are given on an as is basis.

[0084] I. Cationic and/or anionic polymers used in the Examples are:

[0085] a) 10 AETMAC/90 AMD: An aqueous linear cationic copolymer solution of 10 mole % of acryloxyethyltrimethylammonium (AETMAC) chloride and 90 mole a of acrylamide (AMD) of 5,000,000 to 10,000,000 molecular weight having a polymer solids content of 32-33%. Identified as Cat. A.

[0086] b) 70 AMD/30 AA: A linear anionic copolymer of 70.mole percent acrylamide and 30-mole percent acrylic acid (AA) of $15\text{-}20\times10^6$ molecular weight. Identified as An A. An B is 60 mole % NH_4 acrylate/acrylamide polymer and An C is 100 mole % NH_4 acrylate.

[0087] II. Ethyleneimine Polymers used in the Examples are:

[0088] a) PEI-#2: A modified, high molar mass polyethylenimine.

[0089] b) PEI-#1: A commercially available polyethylenimine of 50% solids.

[0090] III. Anionic particles used in the Examples are:

[0091] a) Bentonite: Commercially available anionic swelling bentonite from clays such as sepiolite, at tapulgite or montmorillonite, as described in U.S. Pat. No. 4,305,781.

[0092] b) Silica: Colloidal silica obtained commercially as BMA O colloidal silica as used in the Compozil® system.

[0093] IV. Microbeads used in the Examples are:

[0094] a) 60 AA/40 AMD/2,000 ppm MBA: A microemulsion copolymer of 60 mole % of acrylic acid and 40 mole % of acrylamide, crosslinked with 2,000 ppm of N,N'-methylene-bisacrylamide (MBA) of 180[1] nm particle diameter. The Solution Viscosity (SV) of this material is about 1.4 mPa.s, used as 28% real polymer (Microbead A).

[0095] b) 30 AA/70 AMD/800 ppm MBA: A microemulsion copolymer of 30 mole % acrylic acid and 70 mole % of acrylamide cross-linked with 800 ppm of MBA and of about 180 nm particle diameter. The SV of the material is about 1.6, used as 28% real polymer. (Microbead B)

[0096] The microemulsions may be prepared as described in U.S. Pat. No. 5,167,766; the disclosure of which is expressly incorporated herein by reference thereto.

[0097] V. Vinylamine Polymers used in the Examples are:

[0098] a) PVA-a: A commercially available polyvinylamine polymer powder.

[0099] b) PVA-b: A polyvinylamine homopolymer hydrochloride salt with a molecular weight; of 300-400 k. It is in powder form.

[0100] c) PVA-c: A 50-100K molecular weight version of PVA-b.

[0101] d) PVA-d: A second sample of PVA-b.

[0102] e) PVA-e: A polyvinylamine homopolymer in solution form (15.6% PVA) with a molecular weight of 185-250K. It is in the free base form.

[0103] f) PVA-f:. Sodium formate salt of PVA-e.

[0104] g) PVA-g: A polyvinylamine homopolymer in solution form (6.1%.PVA) with a molecular weight of 560-600K. It is in the free base form.

[0105] h) PVA-h: Sodium formate salt of PVA-g.

[0106] i) PVA-i: A vinylamine terpolymer at 12.7% active contents.

[0107] j) PVA-j: A high molecular weight, low cationicity polyvinylamine emulsion at 22% active content. The CEQ is 0.149×10^{-2} eq/g active and an inherent viscosity of 9.45 dL/g.

[0108] k) PVA-k: A polyvinylamine solution at 11% active content with a CEQ of 0.96×10^{-2} equiv./g active and and inherent viscosity of 1.49 d L/g.

[0109] l) PVA-k2: Like PVA-k but with a CEQ of 0.72×10^{-2} eq/g active and an inherent viscosity of 1.44 dL/g.

EXAMPLE 1

[0110] A simulated alkaline fine paper furnish of 80/20 ratio oz pulp solids (70/30 hardwood/softwood bleached Kraft pulp) to $CaCO_3$ filler is used in this drainage test. It also contains 250 ppm-of SO_4 added as Na_2SO_4, 100 ppm of HCO_3 added as $NaHCO_3$, 50 ppm of Ca added as $CaCl_3$ and 5 pounds of cationic potato starch. The furnish pH is 8.0. To this furnish are added the additives in Table 1.

TABLE I

	Additive	10 × Drainage-sec.
1)	.33 lb. PVA-a	103
	.66 lb. PVA-a	85
	.99 lb. PVA-a	74
2)	.33 lb. PVA-a	57
	2.0 lb. Microbead A	
3)	.66 lb. PVA-a	40
	2.0 lb. Microbead A	
4)	.99 lb. PVA-a	22
	2.0 lb. Microbead A	
5)	.33 lb. PVA-b	102
	.66 lb. PVA-b	85
	.99 lb. PVA-b	82
6)	.33 lb. PVA-b	42
	2.0 lb. Microbead A	
7)	.66 lb PVA-b	27
	2.0 lb Microbead A	

---

[1] The particle diameter in nanometers is defined and used herein as that determined by quasielectric light scattering spectroscopy ("QELS") as carried out on the polymer emulsion, microemulsion or dispersion.

TABLE I-continued

	Additive	10 × Drainage-sec.
8)	.99 lb PVA-b 2.0 lb Microbead	21

[0111] This example clearly shows the enhanced drainage achieved using the process of the present invention, especially as shown in Tests 4 and 8.

EXAMPLE 2

[0112] The procedure of Example 1 is followed with the following results. In this case, the furnish includes 10 pouunds of a cationic potato starch.

Additive with 2 lbs	10 × Drainage-sec. Additive-lbs.			
Microbead A	.33	.66	.99	1.32
PEI # 1	47	42	42	—
PEI # 2	51	49	42	—
PAA · HCl (40% sol.)	69	62	60	59
PVA-b	47	30	21	17
PVA-a	61	38	27	21

The PEI's and PAA are tested on an active solids basis.
PAA = polyallylamine

[0113] The PEI's and PAA are tested on an active solids basis.

[0114] PAA=polyallylamine

[0115] The above results exemplify the superior drainage performance of the PVA/microbead system vis-a-vis polyethylenimine or polyallylamine/microbead systems.

EXAMPLE 3

[0116] Following the procedure of Example 1 the following data are recorded with $CaCO_3$ (30%) used in the furnish instead of 20% (ie., 70/30 pulp/$CaCO_3$ rather then 80/20). The Cat A doses are on an active basis, as are the PEI.

Additive-lbs.	% TW Consistency		
	Bentonite-lbs.		
Cat. A	3.0	5.0	7.0
0.33	0.154	0.147	0.140
0.66	0.133	0.108	0.093
0.99	0.088	0.060	0.057
	Microbead A		
Cat. A (+5. lb alum)	1.0	2.0	30
0.33	0.170	0.120	0.110
0.66	0.134	0.112	0.086
0.99	0.138	0.113	0.081
PVA-b			
.33	0.140	0.093	0.067
.66	0.085	0.050	0.056
.99	0.065	0.047	0.026
PEI-# 1			
.33	0.189	0.167	0.154
.66	0.170	0.153	0.137
.99	0.168	0.150	0.132

[0117] Again, as regards retention, the PVA/microbead system of the present invention clearly outperforms bentonite-based, cationic polymer-based-and polyethylenimine-based systems.

EXAMPLE 4

[0118] Example 3 is again followed but using 5 lbs. of cationic potato starch. The following results are observed.

Additve-lbs.	10 × Drainage-sec. Microbead A-2 lbs
PVA-b	
.33	81
.66	48
.99	27
PVA-c	
.33	74
.66	49
.99	32
PVF	
.33	106
.66	103
.99	105

PVF = (N-polyvinylformamide) powder; 1–4 million molecular weight.

[0119] PVA/microbead systems are shown to outperform a polyvinylformamide/microbead system showing that the amine functionality provides a cooperative effect with the microbead.

EXAMPLE 5

[0120] Again following the procedure of Example 4 except that the PH of the furnish is 8.4, the following results are recorded:

Additive	10 × Drainage-sec			
Alum-5 lbs.	36			
Cat. A-0.66 lb. active				
Microbead A-2 lbs.				
PVA-b	.25 lb	0.5	1.0	1.5
Microbead A-2 lbs.	44	30	18	14
PVA-d	.25 lb	0.5	1.0	1.5

-continued

Additive	10 × Drainage-sec			
Microbead A-2 lbs.	47	33	17	13
PEI-# 1 (active basis)	.25 lb	0.5	1.0	1.5
Microbead A-2 lbs.	42	37	33	31

[0121] The PVA/microbead system of the present invention again is shown to be much superior to cationic polymer-based and polyethylenimine-based systems, elevated pH.

EXAMPLE 6

[0122] Again following the procedure of Example 3 the results below are recorded.

[0123] All amounts of PVA additive are specified in PVA content (ie: free base and not salt) in this and the following Examples.

Additive	10 × Drainage-sec.			
Cat. A-0.66 lb active Bentonite-5 lbs	38			
Alum-0.66 lb active Cat. A-2 lbs Microbead A-2 lbs	35			
Microbead A-2 lbs with	.25 lb	.5 lb	.75 lb	1.0 lb
PVA-e	42	20	16	14
PVA-f	39	23	16	14
PVA-g	35	20	15	13
PVA-h	40	21	15	13
PVA-i (dose on active basis)	62	41	20	24
	0.135 lb.	0.27 lb.	0.405 lb.	
PVA-d	68	39	25	—

[0124] This example shows the superior effect of the instant process even when analogous PVA polymers are employed.

EXAMPLE 7

[0125] Again following the procedure of Example 6 except that the furnish is at pH 8.3, the following data are recorded.

Additive	% First Pass Retention	
blank (none)	68.8	
	Microbead A	
	2 lbs	3 lbs
Alum-5 lbs Cat. A-0.66 lb	81.8	83.4
PVA-g		
.2 lb	81.8	83.4
.4 lb	88.8	91.7
.6 lb	89.6	89.3
.8 lb	96.0	—
1.0 lb	98.6	—
PVA-d		
.2 lb	80.0	82.4
.4 lb	87.5	91.7
.6 lb	91.4	92.9
.8 lb	92.8	—
1.0 lb	92.6	—
PVA-f		
.2 lb	80.0	82.8
.4 lb	90.7	89.0
.6 lb	91.7	90.4
.8 lb	92.1	—
1.0 lb	93.4	—

[0126] Various PVA polymer/microbead systems again are shown as outperforming bentonite-based and cationic polymer-based systems in-retention enhancement.

EXAMPLE 8

[0127] The procedure of Example 5 is again followed (except that the pH of the furnish is 8.2) with the following results.

	HB Consistency - % solids		
Additive	0.24%	0.52%	0.74%
Blank (none)	69.5% FPR*	70.2% FPR	70.8% FPR
Cat. A-0.66 lb Bentonite-5 lbs	87.1	84.8	82.8
Cat. A-0.99 lb Bentonite 7 lbs	91.3	90.0	88.5
Alum-5 lbs Cat. A-0.66 lb Microbead A-2 lbs	85.4	83.5	81.8
Alum-5 lbs Cat. A-0.99 lb Microbead A-3 lbs	90.4	89.6	89.2
Microbead A-2 lbs PVA-d			
0.2 lb	72.9	78.3	80.3
0.4 lb	77.5	84.6	86.4
0.6 lb	82.5	90.6	89.6
0.8 lb	88.8	96.2	93.0
1.0 lb	88.3	96.3	96.2

*First Pass Retention

[0128] The effectiveness of the PVA/microbead systems of the present invention is shown at varying furnish consistencies, especially over 0.24% consistency.

EXAMPLE 9

[0129] When the procedure of Example 6 is again followed, the results below are achieved.

Additive	10 × Drainage-sec.
Blank	130
Cat. A-0.66 lb Bentonite-5 lbs	36
Cat. A-0.99 lb Bentonite 7 lbs	27

-continued

Additive	10 × Drainage-sec.
PVA-d-.6 lb	69
Microbead A-0.5 lb	32
Microbead A-1 lb	22
Microbead A-2 lbs	16
Microbead A-3 lbs	14
Bentonite-3 lbs	37
Bentonite-5 lb	35
Bentonite-7 lb	35
Silica-2 lb	60
Silica-4 lb	58
Silica-6 lb	65
AnA-1 lb	46
AnA-2 lbs	36
AnA-3 lbs	33

[0130] The use of the PVA/microbead systems of this invention is shown to be superior in drainage to PVA/inorganic microparticle systems or PVA/anionic polyacrylamide flocculant systems.

EXAMPLE 10

[0131] Again following the procedure of Example 9,except the pH is 8.1, the following results are achieved.

Additive	10 × Drainage - sec.		
Blank	143		
Alum-5 lbs	36		
Cat. A-0.66 lb			
Microbead A-2 lbs			
Cat. A-0.66 lb	35		
Bentonite-5 lbs			
	Microbead A		
	1 lb	2 lbs	3 lbs
PVA-d-0.6 lb	24	19	16
	Microbead B		
	1 lb	2 lbs	3 lbs
"	31	24	21
	AnA		
	1 lb	2 lbs	3 lbs
"	46	37	35
	AnB		
	1 lb	2 lbs	3 lbs
"	30	26	23
	AnC		
	1 lb	2 lbs	3 lbs
"	32	23	20

[0132] Superior drainage characteristics are again shown by the instant PVA/microbead systems.

EXAMPLE 11

[0133] Using the same furnish as in Example 10, the following results are achieved. The consistency is the same as that typically used in the drainage experiments, (0.35%).

Additive			% FPR		
Blank			66.9		
Alum-5 lbs			80.9		
Cat. A-0.66 lb					
Microbead A-2 lbs					
Alum-5 lbs			88.6		
Cat. A-0.99 lb					
Microbead A-3 lbs					
	.2 lb	.4 lb	.6 lb	.8 lb	1.0 lb
			PVA-h		
Microbead A 2 lbs	84.6	90.6	96.9	98.0	98.6
			PVA-d		
-do-	77.1	88.9	95.4	97.4	97.4
			PVA-f		
-do-	82.3	89.4	95.4	97.4	96.9

[0134] Regardless of the molecular weight of the PVA employed, the systems of the present invention outperform, in retention, prior art systems.

EXAMPLE 12

[0135] The procedure of Example 10 is again followed except that the 30% $CaCO_3$ is replaced by 30% ground $CaCO_3$ and the pH is 8.0 The results are set forth below.

Additive			10X Drainage-sec		
Blank			261		
Cat. A-0.66 lb			79		
Bentonite-5 lbs					
Cat. A-0.99 lb			51		
Bentonite-7 lbs					
Alum-5 lbs			80		
Cat. A-0.66 lb					
Microbead A-2 lbs					
Alum-5 lbs.			55		
Cat. A-0.99 lb					
Microbead A-3 lbs					
Microbead A-2 lbs +	.2 lb	.4 lb	.6 lb	.8 lb	1.0 lb
PVA-h	193	67	35	24	21
PVA-d	175	65	42	28	26
PVA-f	176	72	39	28	23

[0136] The presence of ground calcium carbonate in the furnish is shown to have no effect of the superiority of the instant PVA/microbead additive combination.

EXAMPLE 13

[0137] The procedure of Example 12 is again followed except that the $CaCO_3$ is replaced by 20% clay. Results are shown below.

Additive	10 × Drainage-sec pH-8.0
Blank	175
Alum-5 lbs	40
Cat. A.-0.99 lb Microbead A-3 lbs	
PVA-HCl-2–0.6 lb Microbead A-2 lbs	99
PVA-HCl-2–3 lbs Microbead A-2 lbs	25

[0138] Furnishes containing clay are also shown to be effectively treated in accordance with the instant invention albeit at higher dosages than previously reported.

EXAMPLE 14

[0139] The procedure of Example 1 is again followed except that one additive is added to the pail, one additive system is added to an aliquot of the pail in the jar and the furnish contains 30% $CaCO_3$. The results are set forth below.

Pail	Jar	10 × Drainage-sec
—	Cat. A-0.66 lb/ Microbead A-2 lbs	100
	Test One	
Polyamine-2 lbs	Cat. A-0.66 lb/ Microbead A-2 lbs	70
PEI-# 1-1 lb	Cat. A-0.66 lb/ Microbead A-2 lbs	62
PVA-d-0.6 lb	Cat. A-0.66 lb/ Microbead A-2 lbs	69
Alum-5 lbs	Cat. A-0.66 lb/ Microbead A-2 lbs	61
	Test Two	
—	Alum-5 lbs/ Cat. A-0.66 lb/ Microbead A-2 lbs	49
Polyamine-2 lbs (as is basis)	Alum-5 lbs/ Cat. A-0.66 lb/ Microbead A-2 lbs	56
	Test Three	
—	Polyamine-2 lbs Cat. A-0.66 lb Microbead A-2 lbs	79
—	PEI # 1-1 lb (as is basis) Cat. A-0.66 lb Microbead A-2 lbs	56
—	PVA-d-0.2 lb Cat. A-0.66 lb Microbead A-2 lbs	39
—	PEI # 1-2 lbs Microbead A-2 lbs	69

[0140] The use of a cationic polymer in conjunction with PVA/microbead systems is shown to provide excellent drainage in this and Examples 15 and 16, following.

EXAMPLE 15

[0141] On a separate furnish, the procedure of Example 14 is again followed except that the Ca content of the furnish is 250 ppm instead of 50 ppm. Results are shown below.

Pail	Jar	10 × Drainage-sec
	Test One	
—	Cat. A-0.66 lb Microbead A-2 lbs	98
Polyamine-2 lbs	Cat. A-0.66 lb Microbead A-2 lbs	73
PEI # 1-1 lb	Cat. A-0.66 lb Microbead A-2 lbs	51
PVA-b-0.2 lb	Cat. A-0.66 lb Microbead A-2 lbs	80
Alum-5 lbs	Cat. A-0.66 lb Microbead A-2 lbs	79
	Test Two	
—	Alum-5 lbs Cat. A-0.66 lb Microbead A-2 lbs	65
Polyamine-2 lbs	Alum-5 lbs Cat. A-0.66 lb Microbead A-2 lbs	64
	Test Three	
—	Polyamine-2 lbs Cat. A-0.66 lb Microbead A-2 lbs	85
—	PEI-# 1-1 lb Cat. A-0.66 lb Microbead A-2 lbs	51
—	PVA-d-0.2 lbs. Cat. A-0.66 lb Microbead A-2 lbs	36
	Test Four	
—	PEI-# 1-2 lbs Microbead A-2 lbs	43
—	PVA-d-0.6 lb Microbead A-2 lbs	18

EXAMPLE 16

[0142] Following the procedure of Example 3 except that cationic starch is added as specified.

	10 × Drainage	
	0.6 lb PVA-d 2 lbs Microbead A	0.99 lb Cat. A 7 lbs Bentonite
no starch	22 sec.	35 sec.
Starch added before Cationic Polymer		
10 lbs starch	22 sec.	27 sec.
20 lbs starch	23 sec.	29 sec.
30 lbs starch	26 sec.	35 sec.
50 lbs starch	38 sec.	49 sec.

-continued

	10 × Drainage	
	0.6 lb PVA-d 2 lbs Microbead A	0.99 lb Cat. A 7 lbs Bentonite
Starch added after cationic polymer but before anionic component		
10 lbs	24 sec.	31 sec.
20 lbs	32 sec.	38 sec.
30 lbs	27 sec.	42 sec.
50 lbs	33 sec.	57 sec.

EXAMPLE 17

[0143] Example 14, is again followed with varying amounts of Microbead A being used. The results are set forth below.

Additive	10 × Drainage-sec.	
Blank	105	
Cat. A-0.66 lb Bentonite-5 lbs	32	
Cat. A-0.99 lb Bentonite-7 lbs	22	
Cat. A-0.66 lb Microbead A-2 lbs	74	
Cat. A-0.66 lb Alum-5 lbs Microbead A-2 lbs	32	
Cat. A-0.99 lb Alum-5 lbs Microbead A-3 lbs	24	
PVA-d	Cat A-0.66 lb/ Microbead A-2 lbs	Cat A.-0.99 lb/ Microbead A-3 lbs
0.062 lb.	51	47
0.123 lb.	42	—
0.185 lb.	32	29
0.246 lb.	27	24
0.308 lb.	24	—
0.370 lb.	21	19
0.431 lb.	20	—
0.493 lb.	19	14
0.616 lb.	15	12
0.739 lb.	14	—

[0144] This example exhibits the versatility of the PVA/microbead systems hereof at varying concentrations of PVA.

EXAMPLE 18

[0145] The procedure of Example 17 is again followed in order to ascertain the retention data which is presented below.

	% FPR	
Additive	Ca (50 ppm)	Ca (250 ppm)
Blank	69.6	66.5
Cat. A-0.66 lb Microbead A-2 lbs	74.8	72.0
Alum-5 lbs Cat A-0.66 lb Microbead A-2 lbs	82.5	75.8
Alum-5 lbs Cat A-0.66 lb Microbead A-3 lbs	87.1	79.6
PEI # 1-1 lb Cat. A-0.66 lb Microbead A-2 lbs	84.1	80.0
PVA-d-0.162 lb Cat. A-0.66 lb Microbead A-2 lbs	83.9	81.2
Polyamine-2 lbs Cat. A-0.66 lb Microbead A-2 lbs	81.5	75.6
Microbead A-2 lbs		
PVA-d-0.16 lb	76.6	76.0
PVA-d-0.32 lb	84.7	85.9
PVA-d-0.49 lb	90.5	96.4
PVA-d-0.65 lb	94.4	98.0

[0146] The retention performance of the-PVA/microbead systems is shown to surpass related retention additive systems in this Example regardless of Ca concentration

EXAMPLE 19

[0147] Following the procedure of Example 18 except that the Ca concentration is varied, the following results are achieved when the vinylamine polymer addition sequence is also varied.

	10 × Drainage-sec.	
Additive	50 ppm Ca	250 ppm Ca
	Test One 5 lbs Starch in Stock	
Cat. A-0.66 lb Bentonite-5 lbs	36	53
PVA-d-0.6 lb Microbead A-2 lbs	26	22
	Test Two 5 lbs Starch in Stock-10 lbs in Jar A. First Additive Listed added first	
Cat A-0.66 lb Bentonite-5 lbs	33	73
PVA-d-0.6 lb Microbead A-2 lb	27	28
	B. First Additive Listed Added Last	
Cat. A-0.66 lb Bentonite-5 lbs	39	76
PVA-d-0.6 lb Microbead A-2 lb	27	26
	Test Three No Starch in Stock-15 lbs in Jar A. First Additive Listed Added First	
Cat. A-0.66 lb Bentonite-5 lbs	34	49
PVA-d-0.0 lb Microbead A-2 lbs	27	23

-continued

Additive	10 × Drainage-sec. 50 ppm Ca	 250 ppm Ca
B. First Additive Listed Added Last		
Cat. A-0.66 lb Bentonite-5 lbs	41	77
PVA-d-0.6 lb Microbead A-2 lb	25	27

[0148] Sequence of addition of PVA/microbead system components, with and without starch, is shown to not effect drainage results.

EXAMPLE 20

[0149] In this Example, the furnish comprises slushed newsprint containing 5% clay, 250 ppm of SO_4, 100 ppm of HCO_3, 50 ppm Ca and no calcium carbonate. The pH is 7.0 with a consistency of 0.14%. Results are shown below.

	10X Drainage-sec.				
Additive	.25 lb	.50 lb	.75 lb	1.01 lb	1.25 lb
PEI #1 (active basis)	114	111	100	95	84
PVA-h	122	104	105	88	77
PVA-f	124	107	103	97	85

	Microbead A-1 lb	Microbead A-2 lbs	Microbead A-3 lbs 1
PEI #1-.5 lb	83	73	64
PEI #1-1 lb	55	43	57
PVA-h .5 lb	99	93	86
PVA-h-1 lb	102	96	88

EXAMPLE 21

[0150] The procedure of Example 21 is again followed except that the HB is 0.20% and varying amounts of Ca are added. Results are shown below.

	10 × Drainage-sec		
Additive	Ca-50 ppm	Ca-250 ppm	Ca-500 ppm
PVA-h-0.5 lb	146	117	111
PVA-h-1 lb	97	96	84
PEI # 1-.5 lb	132	113	116
PEI # 1-1 lb	103	99	86
Microbead A-3 lb			
PVA-h-.5 lb	92	101	71
PVA-h-1 lb	52	49	38
PEI # 1-.5 lb	74	60	51
PEI # 1-1.0 lb (active basis)	37	32	30

[0151] Examples 20 and 21 show the effect of PVA/microbead systems on simulated waste furnishes.

EXAMPLE 22

[0152] In this Example, the feed is a furnish take from a commercial paper-making facility having an HB c 0.81% with 0.426% $CaCO_3$, 0.487% fines and 47.4/52.6 pulp/filler ratio. The pH is 7.5-8.0. Results are, as indicated below. The instant PVA/microbead systems are shown to perform well on a one day old mill, furnish.

	Additive	% FPR
1.	Starch-20 lbs Alkyl Ketene Dimer-3 lbs	50.0
2.	Starch-20 lbs Alkyl Ketene Dimer-3 lbs Cat. A-0.44 lb	64.6
3.	Alum-2.5 lbs Cat. A-0.44 lb Starch-20 lbs Microbead A-1.33 lbs	69.8
4.	Same as 3. but 0.88 lb Microbead A	75.3
5.	Same as 3. but 2.6 lb Cat. A	70.6
6.	Same as 3. but 5 lb alum	74.0
7.	Same as 6. but 2.6 lb Microbead A	76.0
8.	Same as 7. but 0.88 lb Cat. A	78.3
9.	PVA-d-0.32 lb Starch-20 lbs Microbead A-2 lbs	65.7
10.	PVA-d-.54 lb Microbead A-2 lbs Starch-20 lbs	68.5
11.	PVA-d-.54 lb Microbead A-2 lbs	67.5

EXAMPLE 23

[0153] Following the procedure of Example 12, except that the pH is 7.5 and no strach is included, the following-results are achieved. The PVA/microbead system of the instant invention provides efficient drainage at concentrations lesser than required with prior systems.

	Additive	10 × Drainage-sec.		
1.	Starch-10 lbs Alum-5 lbs Cat. A-2 lbs Microbead A-0.66 lb	68		
2.	Same as 1. but 0.99 lb Cat. A and 3 lbs Microbead A.	47		
3.	Starch-10 lbs Cat A-0.66 lb Bentonite-5 lbs	69		
4.	Same as 3 but 7 lbs Bentonite and 0.99 lb Cat. A	51		
5.	Starch-10 lbs	Microbead A 2 lbs	Microbead A 3 lbs	Microbead A 4 lbs
	PVA-d-0.54 lb	56	49	45
	PVA-d-1.08 lb	34	27	—

EXAMPLE 24

[0154] The procedure of Example 23 is again followed except retention is tested. The results are shown below and are consistent with those of Example 23 except they relate to retention rather than drainage.

	Additive	% FPR	
1.	Starch-10 lbs Alum-5 lbs Cat. A-0.66 lb Microbead A-2 lbs	67.4	
2.	Same as 1. but 0.99 lb Cat A and 3 lbs Microbead A	77.1	
3.	Starch-10 lbs Cat. A-0.66 lb Bentonite-5 lbs	70.0	
4.	Starch-10 lbs Cat. A-0.99 lb Bentonite-7 lbs	72.1	
5.	Starch-10 lbs	Microbead A 2 lb	Microbead A 3 lb
	PVA-d-0.324 lb	67.4	—
	PVA-d-0.54 lb	57.4	65.0
	PVA-d-1.08 lb	66.6	73.9

EXAMPLE 25

[0155] Example 24 is again followed except that 10 lbs of starch are added in each test before the alum or cationic polymer and the pH is varied. The results are set forth below and show that at lower pH: effectiveness of the PVA/microbead system is reduced, but drainage is still improved over a blank i.e. no additive.

	10X Drainage-sec				
Additive	pH 8.5	pH 8	pH 7.5	pH 7	pH 6.5
Alum-5 lbs Cat. A-0.99 lb Microbead A-3 lbs	37	33	36	39	78
PVA-d-0.6 lb Microbead A-2 lb	19	19	27	48	73

EXAMPLE 26

[0156] In this Example, the pulp feed contains 250 ppm SO_4, 100 ppm HCO_3, 50 ppm Ca but no calcium carbonate. Results are shown below as precipitated $CaCO_3$ (FCC) is added in varying amounts. Ten pounds of cationic potato starch are added before the alum or Cat A. The PVA/microbead system is shown to perform better as PCC content increases.

	10X Drainage-sec							
	0% PCC		10% PCC		30% PCC		50% PCC	
Additive	pH 8	pH 7.5	pH 8	pH 7.5	pH 8	pH 7.5	pH 8	pH 7.5
Alum-5 lbs Cat. A-0.99 lb Microbead A-3 lbs	43	36	36	31	31	31	30	33
PVA-d-0.6 lb Microbead A-3 lbs	67	77	28	32	21	32	18	24

EXAMPLE 27

[0157] Utilizing a mill furnish wherein the paper slurry contains 18% precipitated $CaCO_3$ and has a consistency of 0.58%, the following results are achieved with the varied additives. The pH is 8.0. The results are comparable to the in-use system of the mill using PVA/microbead systems.

Alum	Polymer	Starch	Particle	FPR
—	—	8 lb	—	70.5
—	Cat. A-0.8 lb	8 lb	Bentonite-4 lbs	80.9
—	Cat. A-1.0 lb-	8 lb	Bentonite-4 lbs	84.1
—	"	8 lb	Bentonite-6 lb	86.7
5 lb	Cat. A-0.8 lb	8 lb	Micro-bead A-2 lbs	81.7
5 lb	"	8 lb	Micro-bead A-3 lb	85.5
5 lb	Cat. A-1.0 lb	8 lb	Micro-bead A-2 lb	83.1
5 lb	"	8 lb	Micro-bead A-3 lb	86.7
—	PVA-h-.2 lb	8 lb	Micro-bead A-2 lb	77.1
—	PVA-h-.4 lb	8 lb	Micro-bead A-2 lb	77.8
—	PVA-h-.6 lb	8 lb	Micro-bead A-2 lb	80.5
—	PVA-h-.8 lb	8 lb	Micro-bead A-2 lb	81.6
—	PVA-h-1.0 lb	8 lb	Micro-bead A-2 lb	79.3
—	"	8 lb	Micro-bead A-3 lb	80.7

EXAMPLE 28

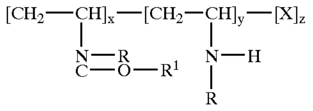
[0158] A 70% pulp/30% precipitated $CaCO_3$ feed containing 250 ppm SO_4, 100 ppm HCO_3 and 50 ppm Ca is used and the drainage determined with various additives according to the present invention. An alkenyl succinic anhydride internal size is also used. The results are shown below. All the systems of the present invention perform well.

	10 x Drainage-sec	
Additive	pH 8.1	pH 7.0
Blank	138	—
Starch-10 lb	40	52
Alum-5 lb		
Cat. A-0.66 lb		
Microbead A-2 lb		
Starch-10 lb		
Alum 5 lb		
Microbead A-2 lb		
PVA-h-.25 lb	36	—
PVA-h-.50 lb	25	—
PVA-h-.75	19	—
PVA-h-1.0 lb	17	39
Starch-1 lb		
Alum 5 lb		
Microbead A-2 lb		
PVA-i-.25 lb	58	—
PVA-i-.50 lb	46	—
PVA-i-.75 lb	35	—
PVA-i-1.0 lb	30	35
Starch-10 lb		
Alum 5 lb		
Microbead A-2 lb		
PVA-j*-.25 lb	56	—
PVA-j*-.50 lb	41	—
PVA-j*-.75 lb	37	—
PVA-j*-1.0 lb	33	37
PVA-k*-.25 lb.	49	—
PVA-k*-.50 lb	32	—
PVA-k*-.75 lb	22	—
PVA-k*-1.0 lb	17	24
PVA-k2*-.25 lb	53	—
PVA-k2*-.50 lb	34	—
PVA-k2*-.75 lb	23	—
PVA-k2*-1.0 lb	21	—

* = active basis

We claim:

1. A method for making a filled or unfilled paper which comprises adding to an aqueous paper-making furnish (i) from about 0.05 to about 20 pounds per ton, based on the dry weight of the furnish solids, of an ionic, organic, cross-linked polymeric microbead and (ii) from about 0.05 to about 20 pounds per ton, same basis, of a polymeric material, or salt or quaternary thereof, having the formula



$$\begin{array}{ccccc} [CH_2-CH]_x & - & [CH_2-CH]_y & - & [X]_z \\ | & & | & & \\ N-R & & N-H & & \\ C-O-R^1 & & | & & \\ & & R & & \end{array}$$

wherein each R or R^1, individually, is hydrogen, or a C_1-C_3 alkyl group, X is the polymerization residue of a copolymerzable monmer or hydrolyzed derivative thereof and mixtures thereof, x and z are, individually, minerals ranging from about 0 to about 99 and y is a numeral ranging from about 1 about 100.

2. The method of claim 1 wherein the furnish is a filled alkaline aqueous paper furnish.

3. The method of claim 2 wherein the furnish is filled with calcium carbonate or a mixture thereof with another filler.

4. The method of claim 1 wherein the microbeads have a diameter of less than about 500 nm.

5. The method of claim 4 wherein the diameter of said microbeads is between about 25-300 nm.

6. The method of claim 1 wherein x and z, are, individually, numerals ranging from about 0 to about 95 and y is a numeral ranging from about 5 to about 100.

7. The method of claim 1 wherein x and z, are, individually, numerals ranging from about 0 to about 75 and y is a numeral ranging from about 25 to about 100.

8. The method of claim 1 wherein R is hydrogen and y is 100.

9. The method of claim 8 wherein the polymeric material is a salt.

10. Paper produced by the method of claim 1.

11. The method of claim 2 wherein both the microbeads are the polymeric material are cationic.

12. The method of claim 11 wherein the microbead and the polymeric material have opposite charges.

13. The method of claim 12 wherein the microbeads are anionic and the polymeric material is cationic.

14. The method of claim 13 wherein x and z are, individually, numerals ranging from about 0 to about 95 and y is a numeral ranging from about 5 to about 100.

15. The method of claim 13 wherein x and z are, individually, numerals ranging from about 0 to about 75 and y is a numeral ranging from about 25 to about 100.

16. The method of claim 13 wherein R is hydrogen and y is 100.

17. The method of claim 13 wherein the polymeric material is a salt.

18. The method of claim 1 which further comprises additionally adding to said furnish from about 1.0 to about 50 pounds per ton, based on the dry weight of said furnish solids, of an organic ionic polysaccharide.

* * * * *