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(54) Title: COMPOSITIONS AND METHODS OF MAKING PAPER PRODUCTS

(57) Abstract: One or more embodiments include methods of making paper, compositions, and the like.



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COMPOSITIONS AND METHODS OF MAKING PAPER PRODUCTS

CLAIM OF PRIORITY TO RELATED APPLICATION

[0001] This application claims priority to co-pending U.S. provisional application entitled "COMPOSITIONS AND METHODS OF MAKING PAPER PRODUCTS" having Serial No.: 61/652,911, filed on May 30, 2012, which is entirely incorporated herein by reference.

BACKGROUND

1. Field of the Art

[0002] The present embodiments relate to paper and paper making.

2. Description of Related Art

[0003] Paper is sheet material containing interconnected small, discrete fibers. The fibers are usually formed into a sheet on a fine screen from a dilute water suspension or slurry. Paper typically is made from cellulose fibers, although occasionally synthetic fibers are used. During the paper making process, water (dewatering) is removed from the cellulose fibers to form a fiber web or sheet. However one of the problems associated with dewatering is that some fibers and paper making additives are inadvertently removed. In an effort to overcome this problem, retention and dewatering agents can be added to the cellulose fibers to improve dewatering and/or retention. Despite known agents that can be used in dewatering and/or retention, there is still a need to provide agents that improve dewatering and/or retention.

SUMMARY

[0004] In view of the foregoing, one or more embodiments include methods of making paper, compositions, and the like.

[0005] At least one embodiment provides a paper or paperboard formed by a method including: treating a cellulosic fiber with a dewatering/ retention system comprising a polyamine polyamidoamine epihalohydrin resin, wherein the dewatering/retention system has one or more of the following: a higher fiber dewatering rate as compared to a paper that has not been treated with the dewatering/retention system or a higher retention of fiber/particulate as compared to a paper that has not been treated with the dewatering/retention system.

[0006] At least one embodiment provides a method of making a paper, including: introducing to a cellulosic fiber a dewatering/retention system comprising a polyamine polyamidoamine epihalohydrin resin and two or more of following components: an aldehyde-functionalized polymer resin, a micropolymer, colloidal silica, a clay-type material, a polyamine, or a starch.

[0007] At least one embodiment provides a composition, including a mixture of a polyamine polyamidoamine epihalohydrin resin and one or more of following components: an aldehyde-functionalized polymer resin, a micropolymer, a silica microparticle, a clay-type material, a polyamine, or a starch.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 graphically illustrates turbidity as a function of multiple dewatering cycles, an exemplary embodiment compared to a blank.

[0009] FIG. 2 graphically illustrates first pass retention and ash retention of various exemplary embodiments as compared to a blank.

[0010] FIG. 3 graphically illustrates the ratio of EPI sites over the product of RSV and PA mass vs. the ratio of EPI mass over PA mass for PAE and PPAE resins.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0011] Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

[0012] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

[0013] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

[0014] All publications and patents cited in this specification are herein incorporated by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present disclosure is not entitled to antedate such publication by virtue of prior disclosure. Further, the dates of publication provided could be different from the actual publication dates that may need to be independently confirmed.

[0015] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

[0016] Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, synthetic organic chemistry, paper chemistry, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

[0017] The examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, *etc.*), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is at or near atmospheric. Standard temperature and pressure are defined as 20 °C and 1 atmosphere.

[0018] It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms

and phrases that shall be defined to have the following meanings unless a contrary intention is apparent.

Definitions

[0019] The term “substituted” refers to any one or more hydrogens on the designated atom or in a compound that can be replaced with a selection from the indicated group, provided that the designated atom's normal valence is not exceeded, and that the substitution results in a stable compound.

[0020] “Acrylamide monomer” refers to a monomer of formula: $H_2C=C(R_1)C(O)NR_2R_3$, where R_1 is H or C_1 - C_4 alkyl, R_2 and R_3 are H, C_1 - C_4 alkyl, aryl or arylalkyl. Exemplary acrylamide monomers include acrylamide and methacrylamide.

[0021] “Aldehyde” refers to a compound containing one or more aldehyde ($-CHO$) groups, where the aldehyde groups are capable of reacting with the amino or amido groups of a polymer comprising amino or amido groups as described herein. Exemplary aldehydes can include formaldehyde, paraformaldehyde, glutaraldehyde, glyoxal, and the like.

[0022] “Aliphatic group” refers to a saturated or unsaturated, linear or branched hydrocarbon group and encompasses alkyl, alkenyl, and alkynyl groups, for example.

[0023] “Alkyl” refers to a monovalent group derived from a straight or branched chain saturated hydrocarbon by the removal of a single hydrogen atom. Exemplary alkyl groups include methyl, ethyl, n- and iso-propyl, cetyl, and the like.

[0024] “Alkylene” refers to a divalent group derived from a straight or branched chain saturated hydrocarbon by the removal of two hydrogen atoms. Exemplary alkylene groups include methylene, ethylene, propylene, and the like.

[0025] “Amido group” and “amide” refer to a group of formula $-C(O)NY_1Y_2$, where Y_1 and Y_2 are independently selected from H, alkyl, alkylene, aryl and arylalkyl.

[0026] “Amino group” and “amine” refer to a group of formula $-NY_3Y_4$, where Y_3 and Y_4 are independently selected from H, alkyl, alkylene, aryl, and arylalkyl.

[0027] “Aryl” refers to an aromatic monocyclic or multicyclic ring system of about 6 to about 10 carbon atoms. The aryl is optionally substituted with one or more C_1 - C_{20} alkyl, alkylene, alkoxy, or haloalkyl groups. Exemplary aryl groups include phenyl or naphthyl, or substituted phenyl or substituted naphthyl.

[0028] “Arylalkyl” refers to an aryl-alkylene-group, where aryl and alkylene are defined herein. Exemplary arylalkyl groups include benzyl, phenylethyl, phenylpropyl, 1-naphthylmethyl, and the like.

[0029] “Alkoxy” refers to an alkyl group as defined above with the indicated number of carbon atoms attached through an oxygen bridge. Exemplary alkoxy groups include methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, s-butoxy, t-butoxy, n-pentoxy, and s-pentoxy.

[0030] “Halogen” refers to fluorine, chlorine, bromine, or iodine.

[0031] “Dicarboxylic acid compounds” includes organic aliphatic and aromatic (aryl) dicarboxylic acids and their corresponding acid chlorides, anhydrides and esters, and mixtures thereof. Exemplary dicarboxylic acid compounds include maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, naphthalenedicarboxylic acid, dimethyl maleate, dimethyl malonate, diethyl malonate, dimethyl succinate, di-isopropyl succinate, dimethyl glutarate, diethyl glutarate, dimethyl adipate, methyl ethyl adipate, dimethyl sebacate, dimethyl phthalate, dimethyl isophthalate, dimethyl terephthalate, dimethyl naphthalenedicarboxylate, dibasic esters (DBE), poly(ethylene glycol) bis(carboxymethyl)ether, succinyl chloride, glutaryl dichloride, adipoyl chloride, sebacyl chloride, sebacate, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, naphthalenedicarboxylate, maleic anhydride, succinic anhydride, glutaric anhydride, phthalic anhydride, 1,8-naphthalic anhydride, and the like.

[0032] In an exemplary embodiment, the “polyalkylene polyamine” can include a polyethylene polyamine, a polypropylene polyamine, a polybutylene polyamine, a polypentylene polyamine, a polyhexylene polyamine, or a mixture thereof. Polyalkylene polyamines, which may be used in the processes of the present disclosure, may be represented as polyamines in which the nitrogen atoms are linked together by groups of formula $\text{—C}_n\text{H}_{2n}\text{—}$ where n is a small integer greater than unity and the number of such groups in the molecule ranges from two up to about eight. The nitrogen atoms may be attached to adjacent carbon atoms in the group $\text{—C}_n\text{H}_{2n}\text{—}$ or to carbon atoms further apart, but not to the same carbon atom. Suitable polyamines which may be used in the processes of the present disclosure include, but are not limited to ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and dipropylenetriamine (DPTA), which can be obtained in reasonably pure form, but also mixtures and various crude polyamine materials. For

example, the mixture of polyethylene polyamines obtained by the reaction of ammonia and ethylene dichloride, refined only to the extent of removal of chlorides, water, excess ammonia, and ethylenediamine, is a satisfactory starting material. The term "polyalkylene polyamine" as used herein includes any of the polyalkylene polyamines referred to above or to a mixture of such polyalkylene polyamines and derivatives thereof. Additional polyamines include bis-hexamethylenetriamine (BHMT), N-methylbis(aminopropyl)amine (MBAPA), aminoethyl-piperazine (AEP), and other polyalkylenepolyamines (*e.g.*, spermine, spermidine). In an exemplary embodiment, the "polyamine" can include an ammonium, an aliphatic amine, an aromatic amine, or a polyalkylene polyamine. In an exemplary embodiment, the polyalkylene polyamine can include a polyethylene polyamine, a polypropylene polyamine, a polybutylene polyamine, a polypentylene polyamine, a polyhexylene polyamine, or a mixture thereof.

[0033] "Polyamidoamine" refers to a condensation product of one or more of the polycarboxylic acids and/or a polycarboxylic acid derivative with one or more of a polyamine.

[0034] "Paper strength" means a property of a paper material, and can be expressed, *inter alia*, in terms of dry strength and/or wet strength. Dry strength is the tensile strength exhibited by the dry paper sheet, typically conditioned under uniform humidity and room temperature conditions prior to testing. Wet strength is the tensile strength exhibited by a paper sheet that has been wetted with water prior to testing.

[0035] As used herein, the terms "paper" or "paper product" (these two terms are used interchangeably) is understood to include a sheet material that contains paper fibers, and may also contain other materials. Suitable paper fibers include natural and synthetic fibers, for example, cellulosic fibers, wood fibers of all varieties used in papermaking, other plant fibers, such as cotton fibers, fibers derived from recycled paper; and the synthetic fibers, such as rayon, nylon, fiberglass, or polyolefin fibers. The paper product may be composed only of natural fibers, only of synthetic fibers, or a mixture of natural fibers and synthetic fibers. For instance, in the preparation of a paper product a paper web or paper material may be reinforced with synthetic fibers, such as nylon or fiberglass. A paper product may be or impregnated with nonfibrous materials, such as plastics, polymers, resins, or lotions. As used herein, the terms "paper web" and "web" are understood to include both forming and formed paper sheet materials, papers, and paper materials containing paper fibers. A paper product

may be a coated, laminated, or composite paper material. A paper product can be bleached or unbleached.

[0036] Paper can include, but is not limited to, writing papers and printing papers (*e.g.*, uncoated mechanical, coated free sheet, coated mechanical, uncoated free sheet, and the like), industrial papers, tissue papers of all varieties, paperboards, cardboards, packaging papers (*e.g.*, unbleached Kraft paper, bleached Kraft paper), wrapping papers, paper adhesive tapes, paper bags, paper cloths, toweling, wallpapers, carpet backings, paper filters, paper mats, decorative papers, saturating and laminating papers, facing papers, disposable linens and garments, and the like.

[0037] Paper can include tissue paper products. Tissue paper products include sanitary tissues, household tissues, industrial tissues, facial tissues, cosmetic tissues, soft tissues, absorbent tissues, medicated tissues, toilet papers, paper towels, paper napkins, paper cloths, paper linens, and the like.

[0038] Common paper products include printing grades (*e.g.*, newsprint, catalog, publication, banknote, document, bible, bond, ledger, stationery), industrial grades (*e.g.*, bag, linerboard, corrugating medium, construction paper, greaseproof, glassine), and tissue grades (sanitary, toweling, condenser, wrapping).

[0039] A tissue paper may be a feltpressed tissue paper, a pattern densified tissue paper, or a high bulk, uncompacted tissue paper. A tissue paper may be characterized as: creped or uncreped; of a homogeneous or multilayered construction; layered or non-layered (blended); and/or one-ply, two-ply, or three or more plies. Tissue paper may include soft and absorbent paper tissue products such as consumer tissue products.

[0040] Paperboard is thicker, heavier, and less flexible than conventional paper. Many hardwood and softwood tree species are used to produce paper pulp by mechanical and chemical processes that separate the fibers from the wood matrix. Paperboard can include, but is not limited to, semichemical paperboard, linerboards, containerboards, corrugated medium, folding boxboard, and cartonboards.

[0041] Paper may refer to a paper product such as dry paper board, fine paper, towel, tissue, and newsprint products. Dry paper board applications include liner, corrugated medium, bleached, and unbleached dry paper board.

[0042] Paper can include carton board, container board, and special board/paper. Paper can include boxboard, folding boxboard, unbleached kraft board, recycled board, food packaging board, white lined chipboard, solid bleached board, solid unbleached board, liquid

paper board, linerboard, corrugated board, core board, wallpaper base, plaster board, book bindery board, woodpulp board, sack board, coated board, and the like.

[0043] “Pulp” refers to a fibrous cellulosic material. Suitable fibers for the production of the pulps are all conventional grades, for example mechanical pulp, bleached and unbleached chemical pulp, recycled pulp, and paper stocks obtained from all annuals. Mechanical pulp includes, for example, groundwood, thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), bleached chemithermomechanical pulp (BCTMP), alkaline peroxide mechanical pulp (APMP), groundwood pulp produced by pressurized grinding, semi-chemical pulp, high-yield chemical pulp and refiner mechanical pulp (RMP). Examples of suitable chemical pulps are sulfate, sulfite, and soda pulps. The unbleached chemical pulps, which are also referred to as unbleached Kraft pulp, can particularly be used.

[0044] “Pulp slurry” refers to a mixture of pulp and water. The pulp slurry is prepared in practice using water, which can be partially or completely recycled from the paper machine. It can be either treated or untreated white water or a mixture of such water qualities. The pulp slurry may contain interfering substances (*e.g.*, fillers). The filler content of paper may be up to about 40% by weight. Suitable fillers are, for example, clay, kaolin, natural and precipitated chalk, titanium dioxide, talc, calcium sulfate, barium sulfate, alumina, satin white or mixtures of the stated fillers.

[0045] “Papermaking process” is a method of making paper products from pulp comprising, *inter alia*, forming an aqueous pulp slurry that can include cellulosic fiber, draining the pulp slurry to form a sheet, and drying the sheet. The steps of forming from the papermaking furnish, draining, and drying may be carried out in any conventional manner generally known to those skilled in the art.

General Discussion

[0046] The various exemplary embodiments described herein include paper materials that may be formed by treating cellulosic fiber or an aqueous pulp slurry, with a dewatering/retention system comprising a polyamine polyamidoamine epihalohydrin resin. In an exemplary embodiment, the treated cellulosic fiber or aqueous pulp slurry may show an improved fiber dewatering rate relative to cellulosic fiber or an aqueous pulp slurry that is not treated. In an exemplary embodiment, the treated cellulosic fiber or aqueous pulp slurry may show an improved fiber retention and/or particulate retention (*e.g.*, fillers and the like) (also referred to herein as “fiber/particulate” retention) in the paper web, relative to cellulosic fiber or an aqueous pulp slurry that is not treated.

[0047] In an exemplary embodiment, the polyamine polyamidoamine epihalohydrin resin can include, for example, those made using one or more processes as described in U.S. Application serial number 13/074,469 and filed on March 29, 2011, which is incorporated herein by reference in its entirety. An exemplary polyamine polyamidoamine epihalohydrin resin can be the reaction product of three components: a polyamine, a polyamidoamine, and an epihalohydrin. In an exemplary embodiment, either or both of the polyamidoamine and the polyamine can include a primary or a secondary amine that can react with epihalohydrin. The epihalohydrin can cross-link the polyamidoamine and the polyamine during the reaction to form the polyamine polyamidoamine epihalohydrin resin, resulting in a branched polymeric structure.

[0048] In an exemplary embodiment, the polyamidoamines can generally be prepared by reacting a polycarboxylic acid and/or a polycarboxylic acid derivative with one or more of the polyamines, such as, for example, those described above. The reactants may be heated to an elevated temperature, for example about 125 to 200° C. The reactants may be allowed to react for a predetermined time, for example about 1 to 10 hours. During the reaction, condensation water may be collected. The reaction may be allowed to proceed until the theoretical amount of water distillate is collected from the reaction. In an exemplary embodiment, the reaction may be conducted at atmospheric pressure.

[0049] In alternative embodiments, the reaction may proceed under a reduced pressure. Where a reduced pressure is employed, a lower temperature of about 75° C to 180° C may be utilized. At the end of this reaction, the resulting product may be dissolved in water at a concentration of about 20 to 90% by weight total polymer solids, or about 30 to 80% by weight total polymer solids, or about 40 to 70% by weight total polymer solids. In the preparation of the polyamidoamines, the molar ratio of the polyamine to the polycarboxylic acid and/or polycarboxylic acid derivative can be about 1.05 to 2.0.

[0050] An exemplary polycarboxylic acid and/or polycarboxylic acid derivatives thereof (*e.g.*, an ester of the polycarboxylic acid, an acid halide of the polycarboxylic acid, an acid anhydride of the polycarboxylic acid, and the like) can include malonic acid, glutaric acid, adipic acid, azelaic acid, citric acid, tricarballic acid (1,2,3-propanetricarboxylic acid), 1,2,3,4-butanetetracarboxylic acid, nitrilotriacetic acid, N,N,N',N'-ethylenediaminetetraacetate, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2,4-benzenetricarboxylic acid (trimellitic acid), 1,2,4,5-benzenetetracarboxylic acid

(pyromellitic acid), a carboxylate ester of any of these, an acid halide of any of these, an acid anhydride of any of these, or a mixture thereof.

[0051] An exemplary ester of polycarboxylic acids can include dimethyl adipate, dimethyl malonate, diethyl malonate, dimethyl succinate, dimethyl glutarate and diethyl glutarate. An exemplary acid anhydride can include succinic anhydride, maleic anhydride, N,N,N',N'-ethylenediaminetetraacetate dianhydride, phthalic anhydride, mellitic anhydride, pyromellitic anhydride, or a mixture thereof. An exemplary acid halide can include adipoyl chloride, glutaryl chloride, sebacoyl chloride, or a mixture thereof.

[0052] An exemplary polyamidoamine can have a molar ratio of polyalkylene polyamine to dicarboxylic acid of about 2:1 to 0.5:1, about 1.8:1 to 0.75:1, or about 1.6:1 to 0.85:1.

[0053] An exemplary polyamidoamine resin can have a reduced specific viscosity of about 0.02 dL/g to 0.25 dL/g, about 0.04 dL/g to 0.20 dL/g, or about 0.06 dL/g to 0.18 dL/g. Reduced specific viscosity (RSV) can be measured using a glass capillary viscometer at 30° C. The efflux time of each sample can be determined three times and the average efflux time calculated. The RSV can be calculated using the following formula (1):

$$RSV = ((t - t_0))/t_0 c \quad (1)$$

where t is the average efflux time of the polyamidoamine sample diluted with 1 M NaCl solution, t_0 is the average efflux time of 1 M NaCl solution, c is the concentration of the diluted polyamidoamine sample, which is 5 g/dL.

[0054] An exemplary epihalohydrin can be a difunctional crosslinker that is used to prepare the polyamine polyamidoamine epihalohydrin resin. An exemplary epihalohydrin can include epichlorohydrin, epifluorohydrin, epibromohydrin, or epiiodohydrin, alkyl-substituted epihalohydrins, or a mixture thereof. An exemplary difunctional crosslinker for preparing the polyamine polyamidoamine epihalohydrin resin is epichlorohydrin.

[0055] An exemplary polyamine polyamidoamine epihalohydrin resin can generally be formed by reacting polyamine, polyamidoamine, and epihalohydrin, in an aqueous medium.

[0056] In an exemplary embodiment, the weight ratio of polyamine to polyamidoamine, can be about 1:100 to 100:1, about 1:50 to 50:1, or about 1:20 to 20:1. In an exemplary embodiment, the reaction temperature can be about 25 to 100°C, about 40 to 90°C, or about 50 to 80°C.

[0057] In an exemplary embodiment, the total solids of the polyamine polyamidoamine epihalohydrin resin can be about 5 to 80%, about 10 to 50%, or about 15 to 30%. In an exemplary embodiment, the pH values of the polyamine polyamidoamine epihalohydrin resin can be about 2 to 10, about 3 to 9, or about 3 to 8. In an exemplary embodiment, the weight average molecular weight of the polyamine polyamidoamine epihalohydrin resin can be about 350 Daltons (Da) to 10 million Da, about 1000 Da to 5 million Da, or about 5000 Da to 3 million Da. In an exemplary embodiment, the Brookfield viscosity of the polyamine polyamidoamine epihalohydrin resin can be about 3 to 1000 cps, about 5 to 500 cps, or about 8 to 300 cps, for a 20% by weight aqueous solution.

[0058] An exemplary polyamine polyamidoamine epihalohydrin resin can have an epihalohydrin/amine (also expressed herein as “epi/amine” or “E/N”) ratio of about 0.8 or less, about 0.5 or less, about 0.45 or less, about 0.4 or less, or about 0.3 or less. The epi/amine ratio is calculated as the molar ratio of epichlorohydrin content to amine content. An exemplary polyamine polyamidoamine epihalohydrin resin has an E/N ratio of about 0.01 to 0.8, about 0.01 to 0.5, about 0.01 to 0.45, about 0.01 to 0.4, or about 0.01 to 0.3.

[0059] Compared to polyamidoamine epihalohydrin, polyamine polyamidoamine epihalohydrin has more primary and/or secondary amine groups per adipic acid group, which can mean that the molecule contains more hydroxyl groups and more pH dependent cationic groups. It should also be noted that a polyamine polyamidoamine epihalohydrin resin has a very high cationic density, which allows the polyamine polyamidoamine epihalohydrin resin to be used as an anionic neutralizer in highly anionic and high conductivity furnishes, conditions in which many other additives lose performance.

[0060] In an exemplary embodiment, a dewatering/retention system may include both a polyamine polyamidoamine epihalohydrin resin (*e.g.*, polyamine polyamidoamine epichlorohydrin (PPAE) resin) and one or more of the following: an aldehyde-functionalized polymer resin, a micropolymer (*e.g.*, a cationic or anionic micropolymer), silica, silica microparticle, or a clay-type material (*e.g.*, bentonite-like swellable natural material). Although not intending to be bound by theory, the components of the dewatering/retention system appear to interact synergistically to provide improved fiber dewatering rate (up to 80%) and/or fiber/particulate retention (up to 70%).

[0061] An exemplary aldehyde-functionalized polymer resin can be produced by reacting a polymer including one or more hydroxyl, amine, or amide groups with one or more aldehydes. An exemplary polymeric aldehyde-functionalized polymer resin can comprise

glyoxylated polyacrylamides, aldehyde-rich cellulose, aldehyde-functional polysaccharides, or aldehyde functional cationic, anionic or non-ionic starches. Exemplary materials include those disclosed in U.S. Pat. No. 4,129,722, which is herein incorporated by reference. An example of a commercially available soluble cationic aldehyde functional starch is Cobond® 1000 marketed by National Starch. Additional exemplary aldehyde-functionalized polymers may include aldehyde polymers such as those disclosed in U.S. Pat. No. 5,085,736; U.S. Pat. No. 6,274,667; and U.S. Pat. No. 6,224,714; all of which are herein incorporated by reference, as well as the those of WO 00/43428 and the aldehyde functional cellulose described in WO 00/50462 A1 and WO 01/34903 A1. An exemplary polymeric aldehyde-functional resins can have a molecular weight of about 10,000 Da or greater, about 100,000 Da or greater, or about 500,000 Da or greater. An exemplary polymeric aldehyde-functionalized resin can have a molecular weight below about 200,000 Da, such as below about 60,000 Da.

[0062] Further examples of aldehyde-functionalized polymers can include dialdehyde guar, aldehyde-functional additives further comprising carboxylic groups as disclosed in WO 01/83887, dialdehyde inulin, and the dialdehyde-modified anionic and amphoteric polyacrylamides of WO 00/11046, each of which are herein incorporated by reference. Another exemplary aldehyde-functionalized polymer is an aldehyde-containing surfactant such as those disclosed in U.S. Pat. No. 6,306,249, which is incorporated herein by reference.

[0063] An exemplary aldehyde-functionalized polymer can have at least about 5 milliequivalents (meq) of aldehyde per 100 grams of polymer, more specifically at least about 10 meq, more specifically about 20 meq or greater, or most specifically about 25 meq, per 100 grams of polymer or greater.

[0064] An exemplary polymeric aldehyde-functionalized polymer can be a glyoxylated polyacrylamide, such as a cationic glyoxylated polyacrylamide as described in U.S. Pat. No. 3,556,932, U.S. Pat. No. 3,556,933, U.S. Pat. No. 4605702, U.S. Pat. No. 7828934, and U.S. Patent Application 20080308242, each of which is incorporated herein by reference. Such compounds include FENNOBOND™ 3000 and PAREZ™ 745 from Kemira Chemicals of Helsinki, Finland, or HERCOBOND™ 1366, manufactured by Hercules, Inc. of Wilmington, Del.

[0065] An exemplary aldehyde functionalized polymer can be a glyoxalated polyacrylamide resin having the ratio of the number of substituted glyoxal groups to the

number of glyoxal-reactive amide groups being in excess of about 0.03:1, being in excess of about 0.10:1, or being in excess of about 0.15:1.

[0066] An exemplary aldehyde functionalized polymer can be a glyoxalated polyacrylamide resin having a polyacrylamide backbone with a molar ratio of acrylamide to dimethyldiallylammonium chloride of about 99:1 to 50:50, about 98:1 to 60:40, or about 96:1 to 75:25. In an exemplary embodiment, the weight average molecular weight of the polyacrylamide backbone can be about 250,000 Da or less, about 150,000 Da or less, or about 100,000 Da or less. The Brookfield viscosity of the polyacrylamide backbone can be about 10 to 10,000 cps, about 25 to 5000 cps, about 50 to 2000 cps, for a 40% by weight aqueous solution.

[0067] In an exemplary embodiment, the weight ratio of the aldehyde-functionalized polymer resin to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:50 to 50:1, or about 1:20 to 20:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0068] An exemplary dewatering/retention system may include both a PPAE resin and one or more flocculants. The flocculants used in the application of this disclosure are high molecular weight water soluble or dispersible polymers which may have a cationic or anionic charge. Nonionic high molecular weight polymers may also be utilized. These polymers may be completely soluble in the papermaking system, or alternatively may be readily dispersible. They may have a branched or cross-linked structure provided that they do not form objectionable "fish eyes", so called globs of un-dissolved polymer on the finished paper. Polymers of these types are readily available from a variety of commercial sources. They are available as dry solids, aqueous solutions, water-in-oil emulsions which when added to water allow the polymer contained therein to rapidly solubilize, or as dispersions of the water soluble or dispersible polymer in aqueous brine solutions. The form of the high molecular weight flocculant used herein is not deemed to be critical so long as the polymer is soluble or dispersible in the furnish.

[0069] Cationic polymer flocculants useful herein are generally high molecular vinyl addition polymers which incorporate a cationic functional group. These polymers are generally homopolymers of water soluble cationic vinyl monomers, or may be copolymers of a water soluble cationic vinyl monomer with a nonionic monomer such as acrylamide or methacrylamide. The polymers may contain only one cationic vinyl monomer, or may

contain more than one cationic vinyl monomer. Alternatively, certain polymers may be modified or derivatized after polymerization such as polyacrylamide by the Mannich reaction to produce a cationic vinyl polymer useful in the disclosure. The polymers may have been prepared from as little as 1 mole percent cationic monomer to 100 mole percent cationic monomer, or from a cationically modified functional group on a post polymerization modified polymer. Most often the cationic flocculants will have at least 5 mole percent of cationic vinyl monomer or functional group, and most preferably, at least 10 weight percent of cationic vinyl monomer or functional group. Suitable cationic vinyl monomers useful in making the cationically charged vinyl addition copolymers and homopolymers of this disclosure will be well known to those skilled in the art. These materials include: dimethylaminoethyl methacrylate (DMAEM), dimethylaminoethyl acrylate (DMAEA), diethylaminoethyl acrylate (DEAEA), diethylaminoethyl methacrylate (DEAEM) or their quaternary ammonium forms made with dimethyl sulfate or methyl chloride, Mannich reaction modified polyacrylamides, diallylcyclohexylamine hydrochloride (DACHA HCl), diallyldimethylammonium chloride (DADMAC), methacrylamidopropyltrimethylammonium chloride (MAPTAC) and allyl amine (ALA). Those skilled in the art of cationic polymer based retention programs will readily appreciate that the selection of a particular polymer is furnish, filler, grade, and water quality dependent. High molecular weight anionic flocculants which may be useful in this disclosure are preferably water-soluble or dispersible vinyl polymers containing 1 mole percent or more of a monomer having an anionic charge.

[0070] Accordingly, these polymers may be homopolymers or water soluble anionically charged vinyl monomers, or copolymers of these monomers with for instance non-ionic monomers such as acrylamide or methacrylamide. Examples of suitable anionic monomers include acrylic acid, methacrylamide 2-acrylamido-2-methylpropane sulfonate (AMPS) and mixture thereof as well as their corresponding water soluble or dispersible alkali metal and ammonium salts. The anionic high molecular weight polymers useful in this disclosure may also be either hydrolyzed acrylamide polymers or copolymers of acrylamide or its homologues, such as methacrylamide, with acrylic acid or its homologues, such as methacrylic acid, or with polymers of such vinyl monomers as maleic acid, itaconic acid, vinyl sulfonic acid, or other sulfonate containing monomers. Anionic polymers may contain sulfonate or phosphonate functional groups or mixtures thereof, and may be prepared by derivatizing polyacrylamide or polymethacrylamide polymers or copolymers. The most preferred high molecular weight anionic flocculants are acrylic acid/acrylamide copolymers,

and sulfonate containing polymers such as those prepared by the polymerization of such monomers as 2-acrylamide-2-methylpropane sulfonate, acrylamido methane sulfonate, acrylamido ethane sulfonate and 2-hydroxy-3-acrylamide propane sulfonate with acrylamide or other non-ionic vinyl monomer. When used herein the polymers and copolymers of the anionic vinyl monomer may contain as little as 1 mole percent of the anionically charged monomer, and preferably at least 10 mole percent of the anionic monomer. Again, the choice of the use of a particular anionic polymer will be dependent upon furnish, filler, water quality, paper grade, and the like.

[0071] Nonionic flocculants useful in the present disclosure may be selected from polyethylene oxide and poly(meth)acrylamide. In addition to the above, it may be advantageous to utilize so called amphoteric water soluble polymers in certain cases. These polymers carry both a cationic and an anionic charge in the same polymer chain.

[0072] The nonionic, cationic, and anionic vinyl polymer flocculants useful herein can generally have a molecular weight of at least 500,000 Daltons, and preferably molecular weights of 1,000,000 Daltons and higher. Water soluble and/or dispersible flocculants useful herein may have a molecular weight of 5,000,000, or higher, for instance in the range of from 10 to 30 million or higher. The polymers of the present disclosure may be entirely water soluble when applied to the system, or may be slightly branched (two-dimensional) or slightly cross linked (three dimensional) so long as the polymers are dispersible in water. The use of polymers which are entirely water soluble are preferred, but dispersible polymers, such as those described in WO 97/16598, may be employed. Polymers useful may be substantially linear as such term is defined in U.S. Pat. No. 4,753,710. The upper limit for molecular weight is governed by the solubility or dispersibility of the resulting product in the papermaking furnish.

[0073] An exemplary silica microparticle can be used in dry powder form (including dry to the touch gels) or in dispersed form. The silica microparticles can include, for example, amorphous silica microparticles or crystalline silica microparticles. The silica microparticles can be, for example, in the form of colloidal silica, colloidal silicic acid, silica sols, fumed silica, agglomerated silicic acid, silica gels, and precipitated silicas, or any combinations thereof. For instance, silica (*e.g.*, amorphous silica nanoparticles and bentonite) can be added separately or as a mixture (*e.g.*, as a suspension). The silica microparticles can be, for example, inorganic silicates, such as aluminum silicates (*e.g.*, kaolin clay). The silica microparticles can be dispersed amorphous silica microparticles. For purposes herein, the

terminology “silica microparticles” means finely divided silica having a particle size according to the present disclosure, and the term encompasses silica primary particles, silica aggregates (i.e., unitary clusters of a plurality of silica primary particles), silica agglomerates (i.e., unitary clusters of a plurality of silica aggregates), individually or in combinations thereof. The silicon-containing microparticles can include, for example, colloidal silica comprising a surface area from 300 m²/g to 1000 m²/g, 500 m²/g to 800 m²/g, or 600 m²/g to 750 m²/g, and an S-value from 80% to 20%, 70% to 30%, or 60% to 40%. For purposes herein, the “surface area” and “S-value” of the silica particles can be determined by respective methods such as described in U.S. Pat. No. 5,603,805, which is incorporated in its entirety by reference herein. The colloidal silica can be aluminate-treated or untreated. The silica microparticles have a dry particle size, for example, of not greater than about 1,000 nm, 1 nm to 750 nm, 2 nm to 500 nm, 3 nm to 500 nm, 4 nm to 100 nm, 5 nm to 50 nm, or 10 nm to 30 nm, on an average or absolute particle size basis. The silica microparticles can have an absolute particle size within one or more of these size ranges. The dry particle size distribution of the silica particles is, for example, such that at least 90%, or at least 95%, or at least 99% up to 100%, have an absolute particle size of less than 1000 nm, or less than 750 nm, or less than 500 nm, or less than 100 nm, or less than 75 nm, or less than 50 nm. The presence of larger sized silicon-containing particles in the wet-end of papermaking is not excluded; however, they are not needed for purposes of obtaining the improved retention and drainage according to the present disclosure. Colloidal silica solutions are frequently commercially supplied as 4% up to 50% by weight dispersions, which typically are diluted for use in processes according to the present disclosure, although not necessarily. A preferred commercial dispersion of silica is available from Eka Chemicals, Inc. (Marietta, Ga.), such as EKA NP series, *e.g.*, Eka NP 890, a high-solids, surface-modified, structured, anionic silica sol for all pH ranges. As indicated, the silica dispersions may be used as received or as diluted for use according to the present disclosure. The concentration of silica microparticles when used in an aqueous silica suspension, colloid, sol, or other dispersion, can be, for example, between about 0.1% and about 20% by weight, or about 5 to about 15% by weight, or other ranges. The viscosity of the aqueous silica suspension can be less than 50 mPa·s (measured using a Brookfield viscometer at 100 rpm). Exemplary paper made in processes according to the present disclosure can include about 0.05 to about 2.5 pounds (lb.) silica microparticles/ton dry fiber, about 0.1 to about 1 lb. silica microparticles/ton dry fiber, or about 0.2 to about 0.8 lb. silica microparticles/ton dry fiber (on a solids/solids basis). The

amount of silica microparticles added, on a solids basis, can be expressed in weight percentage terms, wherein the amount of added silica microparticles can be as low as about 0.0025 wt % of the dry weight of the cellulose fibers, but usually does not exceed about 0.125% by weight. In an exemplary embodiment, an amount of silica microparticles can be about 0.005 wt % to 0.1 wt % of the dry paper weight.

[0074] In an exemplary embodiment, the weight ratio of the silica microparticle to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0075] In an exemplary embodiment, the clay-type material can include clay materials in the smectite group (*e.g.*, sepiolite, attapulgite, and montmorillonite). An exemplary clay-type material can include bentonite or bentonite-type materials or clays. In general, bentonite and bentonite type materials can include montmorillonite, beidellite, nontronite, saponite, sauconite, vermiculite or hectorite, or a chemically modified version of any one of these. Bentonite can include alkaline earth bentonites (*e.g.*, calcium or magnesium bentonite) or bentonite-type clays and chemically modified variants of these (*e.g.*, exchange of calcium for an alkali metal (*e.g.*, sodium, potassium) or ammonium).

[0076] In an exemplary embodiment, the weight ratio of the clay-type material to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0077] In an exemplary embodiment, the micropolymer can include a cationic and/or anionic micropolymer. An exemplary micropolymer can include one or more of the micropolymer described in US Patent 8,038,846, which is included herein by reference. In an exemplary embodiment, the micropolymer can be in one of at least three different forms: emulsion, dispersion, and water-in-water.

[0078] An exemplary emulsion micropolymer can be manufactured by a polymerization process where the reaction occurs in the presence of a small amount of water and an organic solvent, usually oil, as a continuous phase. The reactant monomers, but not the product polymers, are soluble in the organic solvent. As the reaction proceeds and the product polymer chain length increases it migrates to the small water droplets and concentrates within these water droplets. The viscosity of the final product is low, and the resultant polymer is typically of very high molecular weight. When the emulsion is mixed

with additional water, the polymer inverts (the water becomes the continuous phase) and the solution viscosity becomes very high. An exemplary polymer can be anionic or cationic.

[0079] An exemplary dispersion micropolymer can be made by a precipitation polymerization process in which a salt solution acts as both the continuous phase and as a coagulant. Thus, polymerization occurs in a salt solution in which the monomers are soluble, but not the product polymers. Because the polymer is insoluble in the salt solution, it precipitates as discrete particles, which are kept suspended using appropriate stabilizers. The final viscosity of the product is low, enabling ease of handling. The process produces well-defined particles containing polymers of high molecular weight. There are no surfactants or organic solvents (particularly oils) present and the polymers are solubilized by simply mixing with water. An exemplary polymer of this type can be anionic or cationic. The inorganic salt (the coagulant) and high molecular weight polymer interact synergistically. The system can be amphoteric, meaning that when the high molecular weight polymer is anionic, the inorganic, mineral coagulant is cationic. Preferably the high molecular weight polymer is also hydrophobically associative. References describing these types of polymers include U.S. Pat. Nos. 6,605,674, 4,929,655, 5,006,590, 5,597,859, and 5,597,858, each of which is herein incorporated by reference.

[0080] In an exemplary embodiment, water-in-water micropolymers can be made by a polymerization process in which the reaction occurs in a water-organic coagulant mixture (e.g., typically 50:50), in which both the monomers and product micropolymers are soluble. Exemplary organic coagulants can include certain polyamines such as poly(diallyldimethylammonium chloride) (polyDADMAC) or poly(dimethylaminopropyl acrylamide) (polyDIMAPA). The viscosity of the final product is high but lower than solution polymers and the resultant polymer is typically of very high molecular weight. The water-organic coagulant solvent system serves as a viscosity depressor and coagulant. There are no surfactants or organic solvents (oils) present, and the resultant 2-in-1 polymers are solubilized by simply mixing with water. The final product can be considered to be like a high molecular weight polymer dissolved in the organic liquid coagulant. The low molecular weight organic polymer is the continuous phase and a coagulant. The organic coagulant and high molecular weight polymer interact synergistically. An exemplary polymer of this type is usually cationic and hydrophobically associative. Preferably the high molecular weight polymer is hydrophobically associative also. The micropolymers as used herein can be referred to as "solventless," in that no low molecular weight organic solvent (i.e., no oil) is present.

References describing these types of polymers include U.S. Pat. No. 5,480,934 and U.S. Publ. No. 2004/0034145, each of which is incorporated herein by reference.

[0081] An exemplary aqueous solution of the organic micropolymer can have a reduced viscosity greater than or equal to 0.2 deciliters per gram (dl/g), specifically greater than or equal to 4 dl/g. The organic micropolymers exhibit a solution viscosity of greater than or equal to 0.5 centipoise (millipascal-second) and have an ionicity of greater than or equal to 5.0 percent. An exemplary polymer can be liquid, an aqueous, a cationic or an anionic polymer with typical charge densities of between 5 and 75% mole percent, a solid content between 2 and 70%, and viscosities in water at 1% of between 10 and 20,000 mPa sec.

[0082] An exemplary micropolymer can be prepared by initiating polymerization of an aqueous mixture of monomers in an inorganic mineral coagulant salt or an organic coagulant solution to form an organic micropolymer. In particular, the organic micropolymer is prepared by polymerizing a monomer mixture containing at least about 2 mole percent of a cationic or anionic monomer in an aqueous solution of a polyvalent ionic salt or a low molecular weight organic coagulant. The polymerization is carried out in an aqueous solution that can include 1 to 30 percent by weight, based on the total weight of the monomers, of a dispersant polymer, the dispersant polymer being a water-soluble anionic or cationic polymer which is soluble in the aqueous solution of the polyvalent ionic salt or organic coagulant.

[0083] An exemplary polyvalent ionic coagulant salt can be a phosphate, a nitrate, a sulfate, a halide, *e.g.*, chloride, or combinations thereof, in particular aluminum sulfate, polyaluminum chloride (PAC), and silicated polyaluminum chloride. The low molecular weight organic coagulant has an intrinsic viscosity below 4 dl/g, and one or more functional groups such as ether, hydroxyl, carboxyl, sulfone, sulfate ester-, amino, amido, imino, tertiary-amino and/or quaternary ammonium groups. The organic coagulant can be a polyamine such as polyethyleneimine, polyvinylamine, poly(DADMAC), and poly(DIMAPA), amongst others.

[0084] In an exemplary embodiment, the polymerizable monomers are ethylenically unsaturated, and can be selected from the group consisting of acrylamide, methacrylamide, diallyldimethylammonium chloride, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, acrylamidopropyltrimethylammonium chloride, methacrylamidopropyltrimethylammonium

chloride, acrylic acid, sodium acrylate, methacrylic acid, sodium methacrylate, ammonium methacrylate, and the like, and a combination comprising of at least one of the foregoing monomers.

[0085] In an exemplary embodiment, as set forth in U.S. Pat. No. 5,480,934 (which is incorporated herein by reference), a low-viscosity, water-soluble high molecular weight water-in-water polymeric dispersion is prepared by (i) polymerizing a composition comprising 99 to 70 weight % of a water-soluble monomer (a1), from 1 to 30 weight % of a hydrophobic monomer (a2) and, optionally from 0 to 20 weight %, preferably 0.1 to 15 weight % of an amphiphilic monomer (a3), in the presence of at least one polymeric dispersing agent (D) thereby preparing a dispersion of polymer (A); and a second step (ii) of adding at least one polymeric dispersion agent (D), in an aqueous solution, to the dispersion.

[0086] In an exemplary embodiment, the water-soluble monomer (a1) can be sodium (meth) acrylate, potassium (meth)acrylate, ammonium (meth)acrylate, and the like, as well as acrylic acid, methacrylic acid, and/or (meth)acrylic amides such as (meth)acrylic amide, N-methyl(meth)acrylic amide, N,N-dimethyl(meth)acrylic amide, N,N-diethyl(meth)acrylic amide, N-methyl-N-ethyl (meth)acrylic amide, and N-hydroxyethyl(meth)acrylic amide. Still other specific examples of monomers of type (a1) include 2-(N,N-dimethylamino)ethyl (meth)acrylate, 3-(N, N-dimethylamino)propyl (meth)acrylate, 4-(N,N-dimethylamino)butyl (meth)acrylate, 2-(N,N-diethylamino)ethyl (meth)acrylate, 2-hydroxy-3-(N,N-dimethylamino)propyl (meth)acrylate, 2-(N,N,N-trimethyl ammonium)ethyl (meth) acrylate chloride, 3-(N,N,N-trimethylammonium)propyl (meth)acrylate chloride and 2-hydroxy-3-(N,N,N-trimethylammonium)propyl (meth)acrylate chloride, 2-dimethylaminoethyl(meth)acrylic amide, 3-dimethylaminopropyl(meth) acrylic amide, and 3-trimethylammoniumpropyl (meth) acrylic amide chloride. Monomer components (a1) also include ethylerically unsaturated monomers that are capable of producing water-soluble polymers such as vinylpyridine, N-vinylpyrrolidone, styrenesulfonic acid, N-vinylimidazole, diallyldimethylammonium chloride, and the like. Combinations of different water-soluble monomers, listed under (a1) are also possible. To produce the (meth)acrylic amides, see for example, Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 15, pages 346 to 276, 3d edition, Wiley Interscience, 1981. For the preparation of (meth)acrylic ammonium salts see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 15, pages 346 to 376, Wiley Interscience, 1987, which is incorporated herein by reference.

[0087] An exemplary hydrophobic monomer (a2) can include ethylenically unsaturated compounds such as styrene, alpha-methyl styrene, p-methylstyrene, p-vinyltoluene, vinylcyclopentane, vinylcyclohexane, vinylcyclooctane, isobutene, 2-methylbutene-1, hexene-1, 2-methylhexene-1, 2-propylhexene-1, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,3,5-trimethylcyclohexyl (meth)acrylate, cyclooctyl (meth)acrylate, phenyl (meth)acrylate, 4-methylphenyl (meth)acrylate, 4-methoxyphenyl (meth)acrylate, and the like. Other hydrophobic monomers (a2) include ethylene, vinylidene chloride, vinylidene fluoride, vinyl chloride or other mainly (aryl)aliphatic compounds having polymerizable double bonds. Combinations of different hydrophobic monomers (a2) can be used.

[0088] An exemplary amphiphilic monomer (a3) can be a copolymerizable ethylenically unsaturated compound, *e.g.*, an acrylate or methacrylate comprising a hydrophilic group, *e.g.*, a hydroxyl group, a polyethylene ether group, or a quaternary ammonium group, and a hydrophobic group, *e.g.*, a C₈₋₂₂ alkyl, aryl, or arylalkyl group. In order to produce the amphiphilic monomers (a3) see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 1, 3d ed., pages 10330 to 10354 (1978) and vol. 15, pages 346 to 376 (1981), Wiley Interscience, which is incorporated herein by reference. Combinations of different amphiphilic monomers (a3) can be used.

[0089] An exemplary polymeric dispersing agent (D) can be polyelectrolytes with an average molecular weight (mean weight, MW) of less than 5105 Dalton, or polyalkylene ethers that are incompatible with the dispersed polymer (A). The polymeric dispersing agent (D) can be significantly different in its chemical composition and in its average molecular weight MW from the water-soluble polymer that can include the monomeric mix (A). The average molecular weights MW of the polymeric dispersing agents range between 103 to 5105 Dalton, preferably between 10⁴ to 4~10⁵ Dalton ((to determine MW, see H. F. Mark et al., Encyclopedia of Polymer Science and Technology, vol. 10, pages 1 through 19, J. Wiley, 1987), which is incorporated herein by reference).

[0090] An exemplary polymeric dispersing agent (D) contain at least one functional group selected from the group consisting of ether-, hydroxyl-, carboxyl-, sulfone-, sulfate ester-, amino-, amido-, imino-, tertiary-amino- and/or quaternary ammonium groups. An exemplary polymeric dispersing agent (D) can include cellulose derivatives, polyethylene

glycol, polypropylene glycol, copolymers from ethylene glycol and propylene glycol, polyvinyl acetate, polyvinyl alcohol, starch and starch derivatives, dextran, polyvinyl pyrrolidone, polyvinyl pyridine, polyethyleneimine, polyvinyl imidazole, polyvinyl succinimide, polyvinyl-2-methyl succinimide, polyvinyl-1,3-oxazolidone-2, polyvinyl-2-methyl imidazoline, as well as copolymers which, apart from the combinations of monomeric units of the above mentioned polymers, can contain the following monomer units: maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, (meth)acrylic acid, salts of (meth)acrylic acid or (meth)acrylic amide compounds.

[0091] An exemplary polymeric dispersing agent (D) can include polyalkylene ethers such as polyethylene glycol, polypropylene glycol, or polybutylene-1,4-ether. For the production of polyalkylene ethers see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3d ed., vol. 18, pages 616 to 670, 1982, Wiley Interscience. An exemplary polymeric dispersing agents (D) can include polyelectrolytes such as polymers that contain monomer units such as salts of (meth)acrylic acid, anionic monomer units or derivatives quaternated with methyl chloride such as N,N-dimethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate N,N dimethylaminohydroxypropyl(meth)acrylate amide and N,N-dimethylaminopropyl(meth)acrylic amide. An exemplary polymeric dispersing agent can include poly(diallyldimethylammonium chloride) (poly-DADMAC) with an average molecular weight MW between 5×10^4 and 4×10^5 Dalton. For the production of polyelectrolytes see, for example, Kirk-Othmer, Encyclopedia of Chemical Technology, 3d ed., vol. 18, pages 495 to 530, 1982, Wiley Interscience, which is incorporated herein by reference. Furthermore, low molecular emulsifying agents having a molecular weight of less than 10^3 Dalton in quantities of 0 to 5 weight % based on the polymer dispersion can be used.

[0092] These and other solventless polymers are included in the scope of the present disclosure, regardless of the number, types, or concentration of monomers. The micropolymers can also include cationic and anionic organic micropolymers that have been dried to form a powder.

[0093] In an exemplary embodiment, the weight ratio of the cationic or anionic micropolymer to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0094] An exemplary dewatering/retention system may include both a polyamine polyamidoamine epihalohydrin resin (*e.g.*, polyamine polyamidoamine epichlorohydrin (PPAE) resin) and one or more of the following: a cationic coagulant or a starch. Although not intending to be bound by theory, the components of the dewatering/retention system appear to provide increased dewatering and/or retention, while reducing the amount of PPAE used in the dewatering/retention system, as compared to a similar system that does not include this combination. An exemplary cationic coagulant can include both in-organic coagulants and organic coagulants. The in-organic coagulants can include alum, polyaluminum chloride (PAC), and silicate polyaluminum chloride. The organic coagulants can include polyDADMAC, copolymers of DADMAC, cationic polyacrylamide, polyDIMAPA, condensation copolymers of dimethylamine and epichlorohydrin, condensation copolymers of dimethylamine, epichlorohydrin, and ethylene diamine, polyamidoamine epichlorohydrin, polyamine epichlorohydrin, vinylamine-containing polymers, polyethylenimine (PEI), PEI-containing polymers, chitosan, and cationic guar. An exemplary starch can include cationic, anionic, and/or amphoteric starches, which are readily available by derivatization of starch. Examples of starches that can be used include, without limitation, corn, waxy maize, potato, wheat, tapioca, or rice starches, or the like. For most applications, the starch (cationic, anionic and/or amphoteric) has a degree of substitution (DS) of 0.001 to 0.5%. In other applications, the starch has a DS of 0.03 to 0.4%; and in still other applications, the starch has a DS of 0.04 to 0.3.

[0095] In an exemplary embodiment, the weight ratio of the coagulant to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0096] An exemplary starch can include cationic starch, anionic starch, non-ionic starch, amphoteric starch, cross-linked starch, graphed starch, and the like, and combinations of these. An exemplary starch can be selected from a variety of starches, including corn (such as waxy corn or dent corn), potato, sorghum, tapioca, wheat, rice, as well chemically modifications (*e.g.*, cross-linked starch, modifications imparted by modifying temperature and time of processing of the starch, and the like) of these starches, and combinations of these starches. An exemplary starch is a liquid starch.

[0097] In an exemplary embodiment, the weight ratio of the starch to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about

1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0098] An exemplary dewatering/retention system may include a polyamine polyamidoamine epihalohydrin resin (*e.g.*, polyamine polyamidoamine epichlorohydrin (PPAE) resin) and one or more of the following: guar, modified guar, CMC, polyethylene oxide and/or its cofactor, polyvinylpyrrolidone, polyvinylacetate (PVAc), copolymers of vinyl alcohol and vinylacetate, fillers (*e.g.*, PCC, GCC, clay, CaSO₄, talc, TiO₂, aluminum trihydrate, and the like), opacifiers (*e.g.*, organic or inorganic), enzymes, defoamers, biocides (*e.g.*, algacide, fungicide, bacteriacide, and a combination thereof), surfactants, softeners, debonders, bulking agents, wetting agents, FWAs, dyes (*e.g.*, acid, basic, direct, pigment), synthetic fibers, ASA, AKD, rosin (*e.g.*, anionic dispersed, cationic dispersed, soap), paraffin wax, lanoline, stearic acid, SAE, SMA, SAA, MSAA, or PUD, where each of these can be added sequentially, in various combinations, pre-mixed combinations, and the like. In an exemplary embodiment, the weight ratio of any one or a combination of these components to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[0099] An exemplary dewatering/retention system may include a polyamine polyamidoamine epihalohydrin resin (*e.g.*, polyamine polyamidoamine epichlorohydrin (PPAE) resin); optionally, one or more flocculants (*e.g.*, cationic PAM, anionic PAM, nonionic PAM); optionally, one or more of the following: alum, PAC, silicated PAC, polyDADMAC, copolymers of DADMAC, cationic polyacrylamide, polyDIMAPA, condensation copolymers of dimethylamine and epichlorohydrin, condensation copolymers of dimethylamine, epichlorohydrin, and ethylene diamine, polyamidoamine epichlorohydrin, polyamine epichlorohydrin, vinylamine-containing polymers, PEI, PEI-containing polymers, chitosan, and cationic guar; optionally, a starch; optionally, one or more of the following: aldehyde-functionalized polymer resin, a cationic or anionic micropolymer, silica microparticles, or a clay-type material (*e.g.*, bentonite-like swellable natural material); optionally, one or more of the following: guar, modified guar, CMC, polyethylene oxide and/or its cofactor, polyvinylpyrrolidone, PVAc, copolymers of vinyl alcohol and vinylacetate, fillers (*e.g.*, PCC, GCC, clay, CaSO₄, talc, TiO₂, aluminum trihydrate, and the like), opacifiers (*e.g.*, organic or inorganic), enzymes, defoamers, biocides (*e.g.*, algacide, fungicide, bacteriacide, and a combination thereof), surfactants, softeners, debonders, bulking

agents, wetting agents, FWAs, dyes (*e.g.*, acid, basic, direct, pigment), synthetic fibers, ASA, AKD, rosin (*e.g.*, anionic dispersed, cationic dispersed, soap), paraffin wax, lanoline, stearic acid, SAE, SMA, SAA, MSAA, or PUD, each of which has been described herein. In an exemplary embodiment, the weight ratio of any one or a combination of these components to polyamine polyamidoamine epihalohydrin can be about 1:100 to 100:1, or about 1:30 to 30:1, or about 1:10 to 10:1. It should be noted in an exemplary embodiment the ratio can be modified to provide performance and/or cost characteristics, as necessary or desired.

[00100] In an exemplary embodiment, one or more of the dewatering/retention systems provided herein may be added to a pulp slurry, which may be used to produce a paper product. As a result, the dewatering/retention system is dispersed throughout the resultant paper product.

[00101] In an exemplary embodiment, the dewatering/retention system (or one or more components thereof) can be applied as an aqueous solution(s) to the cellulosic fibers, fibrous slurry, or individual fibers. In addition to being applied as an aqueous solution, the dewatering/retention system (or one or more components thereof) can also be applied in the form of a suspension, a slurry, or as a dry reagent depending upon the particular application. An exemplary dewatering/retention system may be provided as a dry reagent, with sufficient water to permit interaction of the components of the dewatering/retention system.

[00102] In an exemplary embodiment, the individual components of the dewatering/retention system may be combined first and then applied to the cellulosic fibers. In an exemplary embodiment, the individual components may be applied sequentially in any order. In an exemplary embodiment, the groups of individual components can be combined and then applied to the cellulosic fibers simultaneously or sequentially.

[00103] By way of example only, application of the dewatering/retention system (or one or more components thereof) can be applied by any of the following methods or combinations thereof.

[00104] An exemplary method can include direct addition of the dewatering/retention system (or one or more components thereof) to a fibrous slurry, such as by injection of the component into a slurry prior to entry into the headbox. In an exemplary embodiment, the slurry can be about 0.05% to about 50%, about 0.1% to 10%, about 0.15% to about 5%, or about 0.2% to about 4%.

[00105] An exemplary method can include spraying the dewatering/retention system (or one or more components thereof) on to a fibrous web. For example, spray nozzles may be

mounted over a moving paper web to apply a desired dose of a solution to a web that can be moist or substantially dry.

[00106] An exemplary method can include application of the dewatering/retention system (or one or more components thereof) by spray or other means to a moving belt or fabric, which in turn contacts the tissue web to apply the chemical to the web, such as is disclosed in WO 01/49937.

[00107] An exemplary method can include printing the dewatering/retention system (or one or more components thereof) onto a web, such as by offset printing, gravure printing, flexographic printing, ink jet printing, digital printing of any kind, and the like.

[00108] An exemplary method can include coating the dewatering/retention system (or one or more components thereof) onto one or both surfaces of a web, such as blade coating, air knife coating, short dwell coating, cast coating, and the like.

[00109] An exemplary method can include extrusion from a die head of the dewatering/retention system (or one or more components thereof) in the form of a solution, a dispersion or emulsion, or a viscous mixture.

[00110] An exemplary method can include application of the dewatering/retention system (or one or more components thereof) to individualized fibers. For example, comminuted or flash dried fibers may be entrained in an air stream combined with an aerosol or spray of the compound(s) to treat individual fibers prior to incorporation into a web or other fibrous product.

[00111] An exemplary method can include impregnation of a wet or dry web with a solution or slurry of dewatering/retention system (or one or more components thereof), where the dewatering/retention system (or one or more components thereof) penetrates a significant distance into the thickness of the web, such as about 20% or more of the thickness of the web, about 30% or more of the thickness of the web, and about 70% or more of the thickness of the web, including completely penetrating the web throughout the full extent of its thickness.

[00112] An exemplary method for impregnation of a moist web can include the use of the Hydra-Sizer® system, produced by Black Clawson Corp., Watertown, N.Y., as described in "New Technology to Apply Starch and Other Additives," Pulp and Paper Canada, 100(2): T42-T44 (February 1999). This system can include a die, an adjustable support structure, a catch pan, and an additive supply system. A thin curtain of descending liquid or slurry is created which contacts the moving web beneath it. Wide ranges of applied doses of the

coating material are said to be achievable with good runnability. The system can also be applied to curtain coat a relatively dry web, such as a web just before or after creping.

[00113] An exemplary method can include a foam application of the dewatering/retention system (or one or more components thereof) to a fibrous web (e.g., foam finishing), either for topical application or for impregnation of the additive into the web under the influence of a pressure differential (e.g., vacuum-assisted impregnation of the foam).

Principles of foam application of additives such as binder agents are described in the following publications: F. Clifford, "Foam Finishing Technology: The Controlled Application of Chemicals to a Moving Substrate," *Textile Chemist and Colorist*, Vol.10, No. 12, 1978, pages 37-40; C. W. Aurich, "Uniqueness in Foam Application," Proc. 1992 *Tappi Nonwovens Conference*, Tappi Press, Atlanta, Georgia, 1992, pp.15-19; W. Hartmann, "Application Techniques for Foam Dyeing & Finishing", *Canadian Textile Journal*, April 1980, p. 55; U.S. Pat. No. 4,297,860, and U.S. Pat. No. 4,773,110, each of which is herein incorporated by reference.

[00114] An exemplary method can include padding of a solution containing the dewatering/retention system (or one or more components thereof) into an existing fibrous web.

[00115] An exemplary method can include roller fluid feeding of a solution of the dewatering/retention system (or one or more components thereof) for application to the web.

[00116] When applied to the surface of a paper web, an exemplary embodiment of the present disclosure may include the topical application of the dewatering/retention system (or one or more components thereof) on an embryonic web prior to Yankee drying or through drying.

[00117] In an exemplary embodiment, the application level of the dewatering/retention system can be about 0.05% to about 10% by weight relative to the dry mass of the web for any of the dewatering/retention systems. In exemplary embodiment, the application level can be about 0.05% to about 4%, or about 0.1% to about 2%. Higher and lower application levels are also within the scope of the embodiments. In some embodiments, for example, application levels of from about 5% to about 50% or higher can be considered.

[00118] An exemplary dewatering/retention system, when combined with the web or with cellulosic fibers, can have any pH, though in many embodiments it is desired that the dewatering/retention system is in solution in contact with the web or with fibers have a pH below about 10, about 9, about 8, or about 7, such as about 2 to about 8, about 2 to about 7,

about 3 to about 6, and about 3 to about 5.5. Alternatively, the pH range may be about 5 to about 9, about 5.5 to about 8.5, or about 6 to about 8. These pH values can apply to the PPAE polymer prior to contacting the web or fibers, or to a mixture of the dewatering/retention system in contact with the web or the fibers prior to drying.

[00119] In an exemplary embodiment, before the dewatering/retention system is applied to an existing web, such as a moist embryonic web, the solids level of the web may be about 10% or higher (*i.e.*, the web comprises about 10 grams of dry solids and 90 grams of water, such as about any of the following solids levels or higher: about 12%, about 15%, about 18%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 60%, about 75%, about 80%, about 90%, about 95%, about 98%, and about 99%, with exemplary ranges of about 30% to about 100% or about 65% to about 90%).

[00120] Ignoring the presence of chemical compounds other than the dewatering/retention system and focusing on the distribution of the dewatering/retention system in the web, one skilled in the art will recognize that the dewatering/retention system (including one or more components and/or derivatives thereof) can be distributed in a wide variety of ways. For example, the dewatering/retention system may be uniformly distributed, or present in a pattern in the web, or selectively present on one surface or in one layer of a multilayered web. In multi-layered webs, the entire thickness of the paper web may be subjected to application of the dewatering/retention system and other chemical treatments described herein, or each individual layer may be independently treated or untreated with the dewatering/retention system and other chemical treatments of the present disclosure. In an exemplary embodiment, the dewatering/retention system is predominantly applied to one layer in a multilayer web. Alternatively, at least one layer is treated with significantly less dewatering/retention system than other layers. For example, an inner layer can serve as a treated layer.

[00121] An exemplary dewatering/retention system may also be selectively associated with one of a plurality of fiber types, and may be adsorbed or chemisorbed onto the surface of one or more fiber types. For example, bleached Kraft fibers can have a higher affinity for the dewatering/retention system than synthetic fibers that may be present.

[00122] In an exemplary embodiment, certain chemical distributions may occur in webs that are pattern densified, such as the webs disclosed in any of the following U.S. Pat. No. 4,514,345; U.S. Pat. No. 4,528,239; U.S. Pat. No. 5,098,522; U.S. Pat. No. 5,260,171; U.S. Pat. No. 5,275,700; U.S. Pat. No. 5,328,565; U.S. Pat. No. 5,334,289; U.S. Pat. No.

5,431,786; U.S. Pat. No. 5,496,624; U.S. Pat. No. 5,500,277; U.S. Pat. No. 5,514,523; U.S. Pat. No. 5,554,467; U.S. Pat. No. 5,566,724; U.S. Pat. No. 5,624,790; and U.S. Pat. No. 5,628,876, the disclosures of which are incorporated herein by reference to the extent that they are non-contradictory herewith.

[00123] In an exemplary embodiment, the dewatering/retention system or other chemicals can be selectively concentrated in the densified regions of the web (*e.g.*, a densified network corresponding to regions of the web compressed by an imprinting fabric pressing the web against a Yankee dryer, where the densified network can provide good tensile strength to the three-dimensional web). This is particularly so when the densified regions have been imprinted against a hot dryer surface while the web is still wet enough to permit migration of liquid between the fibers to occur by means of capillary forces when a portion of the web is dried. In this case, migration of the aqueous solution of dewatering/retention system can move the dewatering/retention system toward the densified regions experiencing the most rapid drying or highest levels of heat transfer.

[00124] The principle of chemical migration at a microscopic level during drying is well attested in the literature. See, for example, A. C. Dreshfield, "The Drying of Paper," *Tappi Journal*, Vol. 39, No. 7, 1956, pages 449-455; A. A. Robertson, "The Physical Properties of Wet Webs. Part I," *Tappi Journal*, Vol. 42, No. 12, 1959, pages 969-978; U.S. Pat. No. 5,336,373, and U.S. Pat. No. 6,210,528, each of which is herein incorporated by reference.

[00125] Without wishing to be bound by theory, it is believed that chemical migration may occur during drying when the initial solids content (dryness level) of the web is below about 60% (*e.g.*, less than any of about 65%, about 63%, about 60%, about 55%, about 50%, about 45%, about 40%, about 35%, about 30%, and about 27%, such as about 30% to 60%, or about 40% to about 60%). The degree of chemical migration can depend, for example, on the surface chemistry of the fibers, the chemicals involved, the details of drying, the structure of the web, and so forth. On the other hand, if the web with a solid contents below about 60% is through-dried to a high dryness level, such as at least any of about 60% solids, about 70% solids, and about 80% solids (*e.g.*, from 65% solids to 99% solids, or from 70% solids to 87% solids), then regions of the web disposed above the deflection conduits (*i.e.*, the bulky "domes" of the pattern-densified web) may have a higher concentration of dewatering/retention system or other water-soluble chemicals than the densified regions, for drying will tend to occur first in the regions of the web through which air can readily pass,

and capillary wicking can bring fluid from adjacent portions of the web to the regions where drying is occurring most rapidly. In short, depending on how drying is carried out, water-soluble reagents may be present at a relatively higher concentration (compared to other portions of the web) in the densified regions or the less densified regions (“domes”).

[00126] An exemplary dewatering/retention system (or one or more components or derivatives thereof) may also be present substantially uniformly in the web, or at least without a selective concentration in either the densified or undensified regions.

[00127] According to an exemplary method, the conditions (*e.g.*, temperature of the pulp slurry, temperature of pre-mixing the components, time of pre-mixing the components, concentration of the paper solution, co-mixing of solids, and the like) of the pulp slurry and process can vary, as necessary or desired, depending on the particular paper product to be formed, characteristics of the paper product formed, and the like. In an embodiment, the temperature of the pulp slurry can be about 10 to 80° C when the dewatering/retention system is added to the pulp slurry. In an embodiment, the process variables may be modified as necessary or desired, including, for example, the temperature of pre-mixing the components, the time of pre-mixing the components, and the concentration of the pulp slurry.

[00128] In various exemplary embodiments a paper may be formed by the treatment of a cellulosic fiber or an aqueous pulp slurry with a dewatering/retention system as described herein. The paper can be formed using one or more methods, including those described herein.

EXAMPLES

[00129] Now having described the embodiments, in general, the examples describe some additional embodiments. While embodiments are described in connection with the examples and the corresponding text and figures, there is no intent to limit embodiments of the disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of exemplary embodiments.

Preparation of polyamidoamines (PA)

[00130] Polyamidoamine was first prepared by a condensation reaction of an excess amount of diethylenetriamine with adipic acid. In particular, diethylenetriamine was added to a three neck flask. Adipic acid was then slowly added to the flask and the reaction mixture heated to 165-170°C and maintained for a period of 5 hours. At the end of the reaction, the

product was diluted with water to adjust the concentration to 60% and the temperature was lowered to room temperature. Table A shows the charge ratios of diethylenetriamine and adipic acid.

Table A. Charge ratios of polyamidoamine (PA)

PA	Diethylenetriamine/adipic acid molar ratio
1	1.4
2	1.6
3	1.8
4	1.0

Preparation of PPAE

[00131] Polyamidoamine, polyamine, and water were first added to a one liter reactor with reflux. The reactor was heated to 70°C and maintained at this temperature throughout the reaction. Epichlorohydrin was then added to the reactor slowly to increase product viscosity. Water was added stepwise during the reaction to reduce the viscosity buildup rate to avoid product gelation. Once the product reached the desired viscosity range, a final charge of water was added to the reactor and the pH was adjusted to around 5.0 using concentrated sulfuric acid (95%). The total solids of the products were around 15%. Table B shows the charge ratios and properties of the PPAE products.

Table B. Charge ratios and properties of PPAE resins

PPAE ID	Polyamidoamine backbone DETA/Adipic ratio	Extra polyamine added	Polyamine/Polyamidoamine weight ratio	Final viscosity (cps)
1	PA 3	TETA	0.05	25
2	PA 3	TETA	0.05	110
3	PA 3	TETA	0.24	5
4	PA 3	TETA	0.24	26
5	PA 3	TETA	0.24	92
6	PA 2	DETA	0.07	52
7	PA 2	DETA	0.07	69
8	PA 2	DETA	0.07	96
9	PA 1	TETA	0.22	24
10	PA 1	TETA	0.22	55
11	PA 1	TETA	0.22	95
13	PA 3	DETA	0.07	26

14	PA 3	DETA	0.07	82
15	PA 3	DETA	0.07	96

Preparation of comparative PAE resins

[00132] Polyamidoamine and water were added to a one liter reactor with reflux. The reactor was heated to 70°C and maintained at this temperature throughout the reaction. Epichlorohydrin was then added to the reactor slowly to increase product viscosity. Water was added stepwise during the reaction to reduce viscosity buildup rate to avoid product gelation. Once the product reached the desired viscosity range, the final charge of water was added to the reactor and the pH was adjusted to around 5.0 using concentrated sulfuric acid (95%). The total solids of the products were around 15%. Table C shows the charge ratios and properties of the Comparative Examples.

Table C. Charge ratios and properties of PAE examples

PAE	Polyamidoamine	Polyamine/polyamidoamine weight ratio	pH	Brookfield viscosity at 23°C (cP)
1	PA 1	1.4	5.0	23
2	PA 1	1.4	5.0	64
3	PA 3	1.8	5.0	7
4	PA 3	1.8	5.0	40
5	PA 3	1.8	5.0	93
6	PA 2	1.6	5.0	37
7	PA 2	1.6	5.0	97
8	PA 2	1.6	5.0	140
9	PA 4	1.0	4.0	90

Epichlorohydrin-reactive sites on polyamidoamine

[00133] The polyamidoamine samples contain both primary amine groups and secondary amine groups. It is commonly accepted that each secondary amine group reacts with one epichlorohydrin molecule, whereas each primary amine group reacts with two epichlorohydrin molecules. Therefore, the total number of epichlorohydrin-reactive sites in a polyamidoamine sample is defined as

$$N = a1 + 2 \times a2 \quad (1)$$

N is the molar quantity of epichlorohydrin-reactive sites, $a1$ is the molar quantity of secondary amine groups, and $a2$ is the molar quantity of primary amine groups. $a1$ and $a2$ are defined as

$$a1 = n \frac{m1}{MW2} \quad (2)$$

$$a2 = \left(\frac{m1}{MW1} - \frac{m2}{MW2} \right) \times 2 \quad (3)$$

where m1 is the mass of polyamine used to prepare the polyamidoamine sample, m2 is the mass of dicarboxylic acid and/or its derivative used to prepare the polyamidoamine sample, MW1 is the formula weight of polyamine, MW2 is the formula weight of dicarboxylic acid or its derivative and n is the number of secondary amines in the polyamine

Reduced specific viscosity of polyamidoamine

[00134] Reduced specific viscosity (RSV) was measured using a glass capillary viscometer at 30° C. The efflux time of each sample was determined three times and the average efflux time was calculated. The RSV was calculated as follows:

$$RSV = (t - t_0)/(t_0 c) \quad (4)$$

[00135] t is the average efflux time of the polyamidoamine sample diluted with 1 M NaCl solution, t_0 is the average efflux time of 1 M NaCl solution, c is the concentration of the diluted polyamidoamine sample which was 5 wt%.

[00136] Table D lists the active polyamidoamine mass (PA mass), the calculated molar quantities of epichlorohydrin-reactive sites on polyamidoamine (EPI sites), the RSVs of the polyamidoamine samples (RSV), and also the mass quantities of charged epichlorohydrin to increase sample final viscosity above 50 cps at 23°C (EPI mass). As shown in Figure 3, the x-axis is the ratio of EPI sites over the product of RSV and PA mass, the y-axis is the ratio of EPI mass over PA mass. For four PAE resins, the correlation between x-axis and y-axis is linear with a R^2 of 0.999. In contrast, the data points for the PPAE resins show a complex non-linear correlation and do not fit the PAE linear correlation. Furthermore, the data points of the PPAE resins are all above the fitted line for the PAE resins, suggesting that a greater amount of epichlorohydrin is required to achieve the desired viscosity range compared to the PAE resins. Theoretically, the ratio of EPI mass over PA mass (y-axis) of the PPAE resins will become infinitely large when the ratio of PA mass over extra polyamine mass becomes infinitely small. Overall, these differences demonstrate that the molecular structure of the PPAE resins is fundamentally different from that of the PAE resins.

Table D. Polyamidoamine mass (PA mass), epichlorohydrin-reactive sites on polyamidoamine (EPI sites), reduced specific viscosity (RSV), and the mass quantities of charged epichlorohydrin to increase sample final viscosity above 50 cps at 23°C (EPI mass)

Name	Chemistry	Backbone DETA/Adipic acid molar ratio	PA mass (g)	EPI sites (mole)	RSV (dL/g)	EPI mass (g)
PAE 2	PAE	1.4	107.7	1.27	0.083	21.5
PAE 5	PAE	1.8	77.0	1.30	0.066	29.3
PAE 7	PAE	1.6	53.6	0.781	0.074	15.4
PAE 9	PAE	1.0	129.6	0.608	0.156	5.3
PPAE 11	PPAE	1.4	58.2	0.690	0.083	24.5
PPAE 8	PPAE	1.6	68.7	1.00	0.074	25.6
PPAE 15	PPAE	1.8	87.2	1.48	0.066	40.4
PPAE 5	PPAE	1.8	82.6	1.40	0.066	48.2

Commercial products from Kemira Chemicals:

- Cationic PAM: copolymer of dimethylaminoethyl acrylate methyl chloride quaternary salt and acrylamide, 10 mol% charge, weight average molecular weight is around 6 Million Da
- Anionic PAM: copolymer of acrylic acid and acrylamide, 30 mol% charge, weight average molecular weight is in the range of 3 to 20 Million Da
- GPAM: glyoxylated cationic polyacrylamide product, cationic charge density = 0.3 meq/g.
- Polyamine: copolymer of dimethylamine, epichlorohydrin, and ethylene diamine, 50%, viscosity = 300 cps.
- PolyDADMAC: polydiallyldimethylammonium chloride, 20%, viscosity = 850 cps.
- Anionic Micropolymer: anionic polyacrylamide micropolymer, 30 mol% anionic charge
- Cationic Micropolymer: cationic polyacrylamide micropolymer, 10 mol% cationic charge
- Silica: colloidal silica suspension, 15 % solids content, S-value = 60-65%.

Test Methods:

[00137] Thick stocks from various paper mills were diluted with white water from various paper mills and/or with lab hardened deionized water adjusted to target pH and conductivity ranges. The PPAE addition rate is based on dry mass of the chemical and dry mass of the material in the pulp furnish. Each additive is sequentially added and mixed at about 1000 to 1200 rpm during about 40 seconds of total mixing time depending on the actual paper mill conditions. Detailed contact times for each additive used are as follows:

@ 0 sec ---- turn on mixer

@ 5 sec ---- coagulants, GPAM, polyamine, polyDADMAC, or PPAE

@ 20 sec ---- polyacrylamide

@ 30 sec ---- micro-particles, micro-polymer

@ 40 sec ---- stop mixing.

[00138] The treated pulp furnish is then added immediately to one or more of the following devices for retention and drainage evaluation:

[00139] (a) Vacuum drainage study: 500 mL of pulp furnish is disposed into a 500-mL Buckner funnel and filtered through a No 4 Whatman filter paper with 25 psi vacuum applied. The amount of time needed to collect 400 mL of filtrate is used as the vacuum drainage time. The turbidity of the filtrate is measured as a retention indicator.

[00140] (b) DSF03 study: 1000 mL of pulp furnish is placed into DFS03 (BTG Americas) drainage device, and then filters through a 60 mesh screen. The amount of the time needed to collect 700 grams of filtrate is used as a measurement of free drainage.

[00141] (c) DDJ study: 1000 mL of pulp furnish is placed into a Dynamic Drainage Jar (DDJ) and filtered through a 125P DDJ screen (76 µm or 200 mesh opening).

Approximately 100 mL of filtrate is collected and filtered through No 40 ashless Whatman filter paper to determine the dry mass of filtrate. This solid consistency is referred to as tray solids or white water solids. This procedure follows the TAPPI standard method T 269 cm-92: Comprehensive retention evaluation for paper machines.

[00142] First Pass Retention (FPR)

[00143] First Pass Retention is an indication of the efficiency of fiber and fines retention in a web of paper as it is being formed. The lab evaluation is simulated by using a DDJ to filter pulp furnish through a 125P screen. It is calculated from the consistency of the pulp furnish added to the DDJ and the consistency of the filtrate. This calculation follows the TAPPI standard method T 269 cm-92. The equation is shown as follows:

$$[00144] \quad FPR = (Consistency_{pulp} - Consistency_{filtrate}) / Consistency_{pulp}$$

[00145] First Pass Ash Retention (FPAR)

[00146] FPAR is an indication of the efficiency of inorganic particles retention in a web of paper as it is being formed. It is calculated from the ash content in the pulp furnish and the ash content from the DDJ filtrate.

[00147] The filter pads from the retention evaluation are ashed in a furnace at 525°C for 45 minutes. This follows TAPPI standard method T 211 om-02: Ash in Wood, Pulp, Paper, and Paperboard: Combustion at 525°C

[00148] The equation for FPAR calculation is shown as follows:

$$[00149] \quad \text{FirstPassAsh Retention} = \frac{\text{AshCons}_{\text{pulp}} - \text{AshCons}_{\text{filtrate}}}{\text{AshCons}_{\text{pulp}}}$$

[00150] Detailed Example Discussion:

[00151] Example 1: PPAE used alone

[00152] The Furnish, white water, used in these examples was 100% recycled fiber from old corrugated container for a packaging grade. The pH of the furnish was between 6.5 to 7.5, and the conductivity was between 1000 to 2000 $\mu\text{S}/\text{cm}$ (low conductivity range). The zeta potential of the fiber as measured with a Mutek ZDT06 was -9.9 mV and cationic demand as measured with a Mutek PCD05 was 376 $\mu\text{Eq}/\text{L}$. All the PPAE samples tested showed improvement on both retention and drainage compared to the blank experiment (with no chemical added). PPAE 2 showed the best overall retention and drainage benefit: 46.9% improvement on drainage and 39.6% improvement on retention over the blank (as calculated from Table 1).

Table 1: Vacuum Drainage & Retention by Turbidity

Experiments	Dosage	Drainage time	Turbidity
	(lb/ton)	(sec)	(ntu)
Blank	/	75.6	235
PPAE 1	1	53.4	200
PPAE 1	2	45.2	159
PPAE 1	3	41.3	138
PPAE 2	1	54.1	205
PPAE 2	2	45.6	165
PPAE 2	3	40.2	142
PPAE 3	1	68.8	221
PPAE 3	2	67.0	200
PPAE 3	3	58.1	192
PPAE 4	1	65.2	207
PPAE 4	2	50.8	168
PPAE 4	3	40.9	144
PPAE 5	1	57.8	210
PPAE 5	2	49.2	172
PPAE 5	3	44.8	163

Example 2: The synergistic effect when PPAE is used with Anionic PAM

[00153] The Furnish used was 100% recycled fibers from old corrugated container for a packaging grade, mid ply (filler grade). The pH of the furnish was about 6.5 to 7.5, and the conductivity was about 1000 to 2000 $\mu\text{S}/\text{cm}$ (low conductivity range). The zeta potential of the fiber was -4.4 mV. When used together with 1.0 lb/ton of anionic PAM, 2 lb/ton PPAE 2 increased vacuum drainage 29.7% over the control, as calculated from Table 2.

Table 2: Vacuum Drainage Results

Experiments	Drainage time (sec) without 1.0 lb/ton anionic PAM	Drainage time with 1.0 lb/ton anionic PAM
Blank	95.8	91.6
2.0 lb/ton of PPAE 6	79.5	67.3
2.0 lb/ton of PPAE 2	78.4	68.7

Example 3: PPAE used with cationic polymer and/or microparticles

[00154] [00155] This example demonstrates the synergistic effect of PPAE with a microparticle program (polyacrylamide together with microparticles or micropolymer). The Furnish used was 100% recycled fiber for paperboard. The pH of this furnish was in the range of 6.5 to 7.5, and the conductivity was in the range of 1000 to 2000 $\mu\text{S}/\text{cm}$ (low conductivity range). The fiber charge of this stock was -12.7 mV, and the cationic demand was 405 $\mu\text{Eq}/\text{L}$. Vacuum drainage and filtrate turbidity were used to conduct the evaluation. PPAE 6 showed a synergistic effect when used with CPAM, colloidal silica, and anionic micropolymer.

Table 3A: Vacuum Drainage and Turbidity Results

Experiments	2.0 lb/ton of PPAE 6	
	Drainage time (sec)	Turbidity (ntu)
Blank – No Additive	205	655
1.0 lb/t of CPAM + 1.0 lb/t of silica	95	569
2.0 lb/ton PPAE 6 + 1.0 lb/ton of Cationic PAM + 1.0 lb/ton Colloidal Silica	54	203
1.0 lb/t of CPAM + 1.0 lb/t of Anionic Micropolymer	119	421
2.0 lb/ton PPAE 6 + 1.0 lb/ton of CPAM + 1.0 lb/ton Anionic Micropolymer	107	342

[00156] PPAE 6 used together with 1.0 lb/ton cationic polyacrylamide or 1.0 lb/ton cationic micropolymer was also compared to various other common commercially used retention and drainage aids. PPAE 6 out-performed all other types of retention and drainage aids tested as shown in Table 3B.

Table 3B: Vacuum Drainage and Turbidity Results

Additive 1	Dose	Additive 2	Dose	Drainage	Turbidity
	(lb/ton)		(lb/ton)	(seconds)	(NTU)
/	/	/	/	205	655
NA	NA	Cationic PAM	1	84	473
PPAE 6	2	Cationic PAM	1	54	392
PPAE 6	4	Cationic PAM	1	47	253
GPAM	4	Cationic PAM	1	63	286
Polyamine	4	Cationic PAM	1	93	429
PolyDADMAC	4	Cationic PAM	1	75	439
/	/	Cationic Micropolymer	1	106	584
PPAE 6	2	Cationic Micropolymer	1	68	418
PolyDADMAC	2	Cationic Micropolymer	1	94	575

[00157] Example 4: PPAE used on virgin fiber furnish

[00158] The Furnish used was a 100% bleached virgin fibers used to make light-weight coated paper. The pH of the Furnish was about 7.0 to 8.5, and the conductivity was about 1000 to 2000 $\mu\text{S}/\text{cm}$ (low conductivity range). The cationic demand of the process water was about 640 $\mu\text{Eq}/\text{L}$.

[00159] Free drainage and tray solids were tested and first pass retention was calculated. PPAE 6 as tested showed a significant improvement on drainage (up to 34.0% reduction on drainage time and 59.2% reduction on tray solids for as calculated from Table 4A).

Table 4A: Free Drainage and First Pass Retention with PPAE used alone

PPAE	Dose (lb/ton)	Drainage time (sec)	First Pass Retention
Blank	0	66.7	63%
PPAE 6	2	55.0	81%
PPAE 6	4	53.4	82%

[00160] The synergistic effect was also demonstrated when PPAE 6 was used with Cationic PAM (Table 4B). The drainage time decreased by 40% over the control (Cationic PAM only) and by 55% over the blank. The first pass retention increased by 4.3% over the control and by 15.9% over the blank.

Table 4B: Free Drainage and First Pass Retention

Additives	Drainage (sec)	First Pass Retention
Blank	67.6	63%
1.0 lb/ton of Cationic PAM	49.9	70%
2.0 lb/ton of PPAE 6 + 1.0 lb/ton of Cationic PAM	30.4	73%

[00161] Example 5: PPAE used in an acidic condition

[00162] This example also compared PPAE with other commonly used paper making process retention and drainage aids. The Furnish used was 100% recycled fiber for paperboard. The pH of this furnish was about 4 to 6.5, and the conductivity was about 1000 to 2500 $\mu\text{S}/\text{cm}$. Vacuum drainage and tray turbidity were tested on this stock.

[00163] PPAE 6 showed retention and drainage improvement on this furnish (up to 30.7% reduction on drainage time and 16.0% reduction on filtrate turbidity versus the blank as calculated from Table 5) and surpassed the performance of other chemicals tested such as PEI and polyamine. When used with cationic polyacrylamide, the drainage time was reduced to about 45.7% of the control (cationic polyacrylamide only) and 54.3% of the blank (no additives). The turbidity of the filtrate was reduced 23.8% compared to the control and 24.8% compared to the blank experiment.

[00164] PPAE 6 also showed synergistic effects when used with cationic micropolymer. The drainage time was reduced 26.3% and the turbidity of filtrate was deduced about 5.2% compared to PPAE 6 alone.

Table 5: Vacuum Drainage and Turbidity Results

Additive 1	Dosage	Additive 2	Dosage	Drainage	Turbidity
	(lb/ton)		(lb/ton)	sec	ntu
Blank		/	/	161	43.1
PPAE 6	4	/	/	114	36.2
GPAM	4	/	/	144	89.0
polyamine	4	/	/	148	47.5

/	/	Cationic PAM	1	131	42.5
Polyamine	2	Cationic PAM	1	144	89
PPAE 6	2	Cationic PAM	1	76	49.8

[00165] Example 6: PPAE and synergy in a low conductivity system

[00166] The Furnish used was 100% recycled fibers for paperboard. The Furnish was prepared from thick stock and white water from the same paper machine. The pH of this furnish was about 7.1, and the conductivity was in the range of 1000 to 2500 $\mu\text{S}/\text{cm}$.

Vacuum drainage and tray turbidity were used to conduct the evaluation.

[00167] When used by itself, PPAE 8 repeatedly showed a drainage and retention benefit. Synergistic retention and drainage improvement was also demonstrated for PPAE 8 with cationic polyacrylamide (CPAM), with CPAM and colloidal silica, with CPAM and anionic micropolymer (MP), and with cationic micropolymer as shown in Table 6.

Table 6: Vacuum Drainage and Turbidity of PPAE 8

Additive 1	Dose	Additive 2	Dosage	Additive 3	Dosage	Drainage	Turbidity
	(lb/ton)		(lb/ton)		(lb/ton)	(second)	(ntu)
/	/	/	/	/	/	236	630
PPAE 8	2	/	/	/	/	146	439
/	/	Cationic PAM	1	/	/	94	510
PPAE 8	2	Cationic PAM	1	/	/	82	400
/	/	Cationic Micropolymer	1	/	/	114	503
PPAE 8	2	Cationic Micropolymer	1	/	/	105	363
/	/	Cationic PAM	1	Colloidal Silica	1	140	516
PPAE 8	2	Cationic PAM	1	Colloidal Silica	1	79	328
/	/	Cationic PAM	1	Anionic Micropolymer	1	137	433
PPAE 8	2	Cationic PAM	1	Anionic Micropolymer	1	107	355

[00168] Example 7: PPAE and synergy in a high conductivity pulp furnish

[00169] The Furnish used for testing was from the same thick stock as Example 6, and the white water used to dilute the thick stock was from a different mill manufacturing a similar paper grade, but with significantly higher conductivity. The pH of the final furnish was about 7.1 and the conductivity was about 8000 $\mu\text{S}/\text{cm}$. The fiber charge of this Furnish

was in the range of 8.0 to 10 mV and the cationic demand was 1816 $\mu\text{Eq./L}$. Vacuum drainage and filtrate turbidity were used to conduct the evaluation. In this evaluation, blends of PPAE with polyamine and with liquid starch were also tested.

[00170] When used alone, PPAE 8 showed drainage and retention improvements compared to the blank experiment (Table 7). A synergistic retention and drainage improvement was also found when used with cationic micropolymer (MP), with cationic polyacrylamide (CPAM) and colloidal silica, and with colloidal silica alone.

Table 7: Vacuum Drainage and Turbidity Results of PPAE 8

Additive 1	Dose	Additive 2	Dose	Additive 3	Dose	Drainage	Turbidity
	(lb/ton)		(lb/ton)		(lb/ton)	Second	Ntu
/	/	/	/	/	/	204	695
PPAE 8	2	/	/	/	/	136	456
/	/	Cationic Micropolymer	1	/	/	158	439
PPAE 8	2	Cationic Micropolymer	1	/	/	123	353
/	/	Cationic PAM	1	Colloidal Silica	1	76	527
PPAE 8	2	Cationic PAM	1	Colloidal Silica	1	68	302
/	/	/	/	Colloidal Silica	1	201	673
PPAE 8	2	/	/	Colloidal	1	104	352

[00171] It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (*e.g.*, 1%, 2%, 3%, and 4%) and the sub-ranges (*e.g.*, 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term “about” can include traditional rounding according to the numerical value provided and the

technique/system/apparatus used. In addition, the phrase “about ‘x’ to ‘y’” includes “about ‘x’ to about ‘y’”.

[00172] It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are merely set forth for a clear understanding of the principles of this disclosure. Many variations and modifications may be made to the above-described embodiment(s) of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

CLAIMS

We claim at least the following:

1. A paper or paperboard formed by a method comprising:
treating a cellulosic fiber with a dewatering/retention system comprising a polyamine polyamidoamine epihalohydrin resin, wherein the dewatering/retention system has one or more of the following: a higher fiber dewatering rate as compared to a paper that has not been treated with the dewatering/retention system or a higher retention of fiber/particulate as compared to a paper that has not been treated with the dewatering/retention system.
2. The paper of claim 1, wherein the polyamine polyamidoamine epihalohydrin resin is about 0.01 to 2 wt. % of an aqueous pulp slurry that includes the cellulosic fiber.
3. The paper of claim 1, wherein the dewatering/retention system comprises an aldehyde-functionalized polymer resin.
4. The paper of claim 3, wherein the weight ratio of aldehyde-functionalized polymer resin to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
5. The paper of claim 1, wherein the dewatering/retention system comprises a micropolymer.
6. The paper of claim 5, wherein the weight ratio of micropolymer to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
7. The paper of claim 1, wherein the dewatering/retention system comprises silica microparticles.
8. The paper of claim 7, wherein the weight ratio of colloidal silica to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
9. The paper of claim 1, wherein the dewatering/retention system comprises a clay-type material.

10. The paper of claim 9, wherein the weight ratio of clay-type material to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
11. The paper of claim 1, wherein the dewatering/retention system comprises a coagulant.
12. The paper of claim 11, wherein the weight ratio of the coagulant to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
13. The paper of claim 1, wherein the dewatering/retention system comprises a starch.
14. The paper of claim 13, wherein the weight ratio of the starch to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
15. The paper of claim 1, wherein the dewatering/retention system comprises a flocculent.
16. The paper of claim 15, wherein the weight ratio of the flocculent to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
17. The paper of claim 1, wherein the dewatering/retention system comprises two or more of following: an aldehyde-functionalized polymer resin, a micropolymer, a silica microparticle, a clay-type material, a polyamine, a polyacrylamide, or a starch.
18. The paper of claim 1, wherein the paper is a paper product that is selected from the group consisting of a dry paperboard, a fine paper, a towel, a tissue, and a newsprint product.
19. A method of making a paper, comprising:
introducing to a cellulosic fiber a dewatering/retention system comprising a polyamine polyamidoamine epihalohydrin resin and two or more of following components: an aldehyde-functionalized polymer resin, a micropolymer, colloidal silica, a clay-type material, a polyamine, or a starch.

20. The method of claim 19, wherein one or more of the components and the polyamine polyamidoamine epihalohydrin resin are mixed together prior to being mixed with the cellulosic fiber.
21. The method of claim 19, wherein one or more of the components and the polyamine polyamidoamine epihalohydrin resin are added to the cellulosic fiber simultaneously.
22. The method of claim 19, wherein one or more of the components and the polyamine polyamidoamine epihalohydrin resin are added to the cellulosic fiber sequentially.
23. The method of claim 19, wherein the weight ratio of one or more components to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
24. The method of claim 19, wherein the paper is a paper product that is selected from the group consisting of a dry paper board, a fine paper, a towel, a tissue, and a newsprint product.
25. A composition, comprising a mixture of a polyamine polyamidoamine epihalohydrin resin and one or more of following components: an aldehyde-functionalized polymer resin, a micropolymer, a silica microparticle, a clay-type material, a polyamine, or a starch.
26. The composition of claim 25, wherein the weight ratio of the one or more components to polyamine polyamidoamine epihalohydrin resin is about 1:100 to about 100:1.
27. The composition of claim 25, wherein the polyamine polyamidoamine epihalohydrin resin is the reaction product of: a polyamidoamine, a first polyamine, and an epihalohydrin; wherein the polyamidoamine is prepared by a process comprising reacting a polycarboxylic acid, a polycarboxylic acid derivative, or a combination thereof with a second polyamine to form the polyamidoamine, wherein a molar ratio of the second polyamine to the polycarboxylic acid, polycarboxylic acid derivative, or a combination thereof, is about 1.05 to about 2.0.
28. The composition of claim 27, wherein the polycarboxylic acid and the polycarboxylic acid derivative are independently selected from the group consisting of: malonic acid, glutaric acid, adipic acid, azelaic acid, citric acid, tricarballic acid (1,2,3-

propanetricarboxylic acid), 1,2,3,4 butanetetracarboxylic acid, nitrilotriacetic acid, N,N,N',N'-ethylenediaminetetraacetate, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2,4-benzenetricarboxylic acid (trimellitic acid) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid), dimethyl adipate, dimethyl malonate, diethyl malonate, dimethyl succinate, dimethyl glutarate, diethyl glutarate, succinic anhydride, maleic anhydride, N,N,N',N'-ethylenediaminetetraacetate dianhydride, phthalic anhydride, mellitic anhydride, pyromellitic anhydride, adipoyl chloride, glutaryl chloride, sebacoyl chloride, and a mixture thereof.

29. The composition of claim 27, wherein the polyamine polyamidoamine epihalohydrin resin has a weight average molecular weight of 350 Daltons (Da) to 10 million Da.

30. The composition of claim 27, wherein the first polyamine and the second polyamine are independently selected from the group consisting of: ammonium, urea, aliphatic amines, aromatic amines, ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), dipropylenetriamine (DPTA), bis-hexamethylenetriamine (BHMT), N-methylbis(aminopropyl)amine (MBAPA), aminoethyl-piperazine (AEP), pentaethylenhexamine (PEHA), and a mixture thereof.

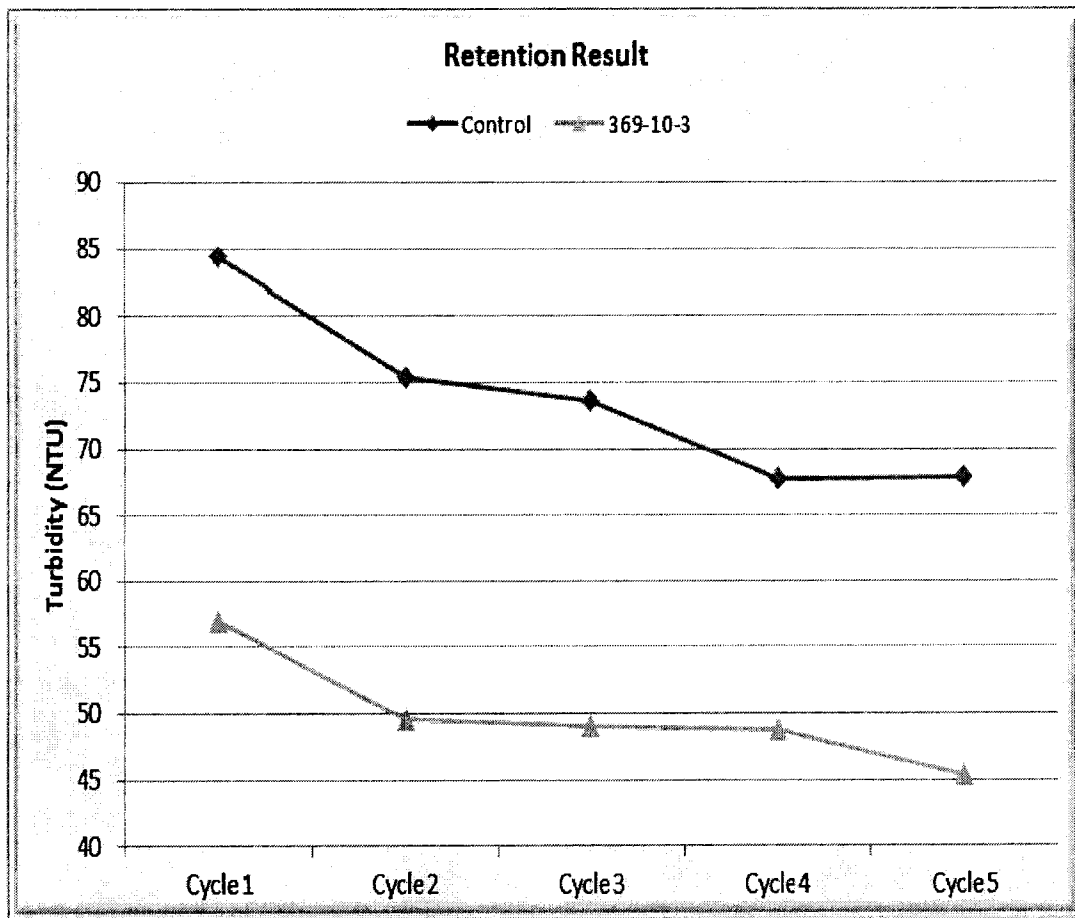
31. The composition of claim 27, wherein the weight ratio of the second to the polyamidoamine is about 1:100 to about 100:1.

32. The composition of claim 19, wherein the aldehyde-functionalized polymer resin is a cationic or an anionic polyacrylamide resin.

33. The composition of claim 19, wherein the micropolymer is a cationic micropolymer or an anionic micropolymer.

34. The composition of claim 19, wherein the clay-type material is bentonite or talc.

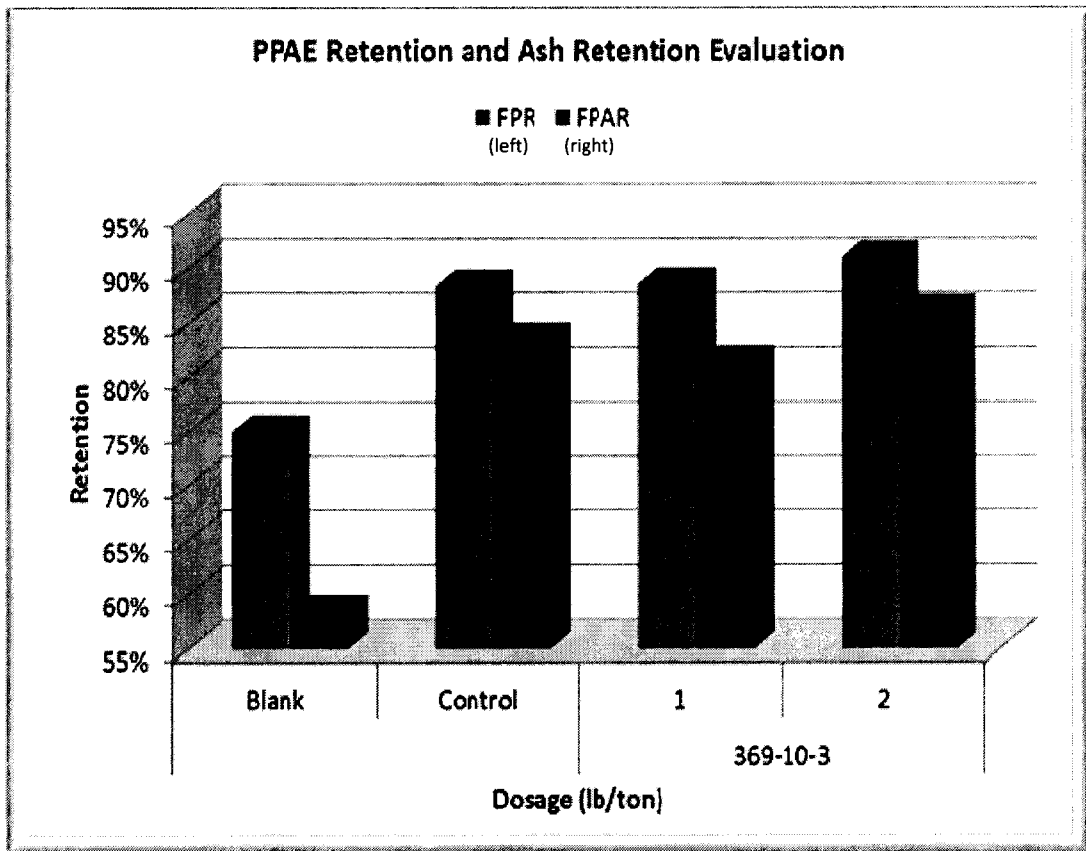
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Recirculation Study Turbidity Results

FIG. 1

2/3



First Pass Retention and Ash Retention

FIG. 2

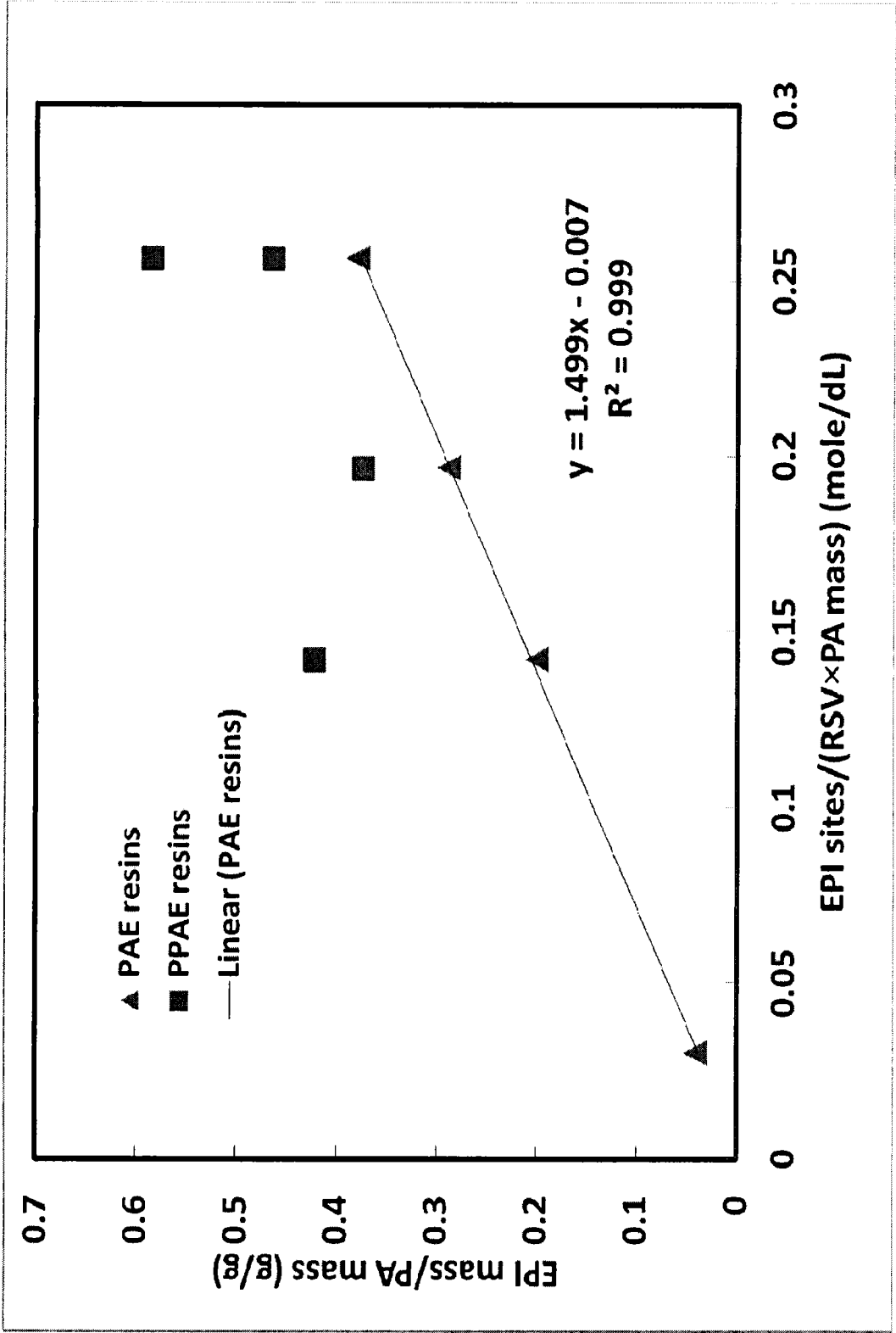


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2013/001497

A. CLASSIFICATION OF SUBJECT MATTER INV. D21H17/37 D21H17/28 D21H17/55 D21H17/56 D21H17/68 D21H21/10 ADD. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D21H Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EP0-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">22 October 2013</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">30/10/2013</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Karlsson, Lennart</div>

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