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(54) Title: PROCESS TO ENHANCING DRY STRENGTH OF PAPER BY TREATMENT WITH VINYLAMINE-CONTAINING POLYMERS AND ACRYLAMIDE CONTAINING POLYMERS

(57) Abstract: A process is disclosed for the production of paper with enhanced dry strength comprising adding to the wet end of a paper machine, (a) a vinylamine-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 750,000 daltons and (b) an amphoteric or cationic acrylamide-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 1,500,000 daltons, wherein the sum of the anionic and cationic monomers comprises at least 5% on a molar basis of the composition of the acrylamide-containing polymer.

PROCESS FOR ENHANCING DRY STRENGTH OF PAPER BY TREATMENT WITH
VINYLAMINE-CONTAINING POLYMERS AND ACRYLAMIDE-CONTAINING
POLYMERS

FIELD OF THE INVENTION

[0001] This invention relates to enhanced dry strength in paper using a process of treating a pulp slurry with a combination of a vinylamine-containing polymer and a cationic or amphoteric acrylamide-containing polymer.

BACKGROUND OF THE INVENTION

[0002] The papermaking industry is constantly seeking new synthetic additives to improve the dry strength of paper products. Improved dry strength can give a higher performance product, but also may allow the papermaker to use less cellulosic fiber to achieve a particular performance target. Furthermore, the increased usage of recycled fiber results in a weaker sheet, forcing the papermaker to either increase basis weight of the sheet or employ synthetic strength additives. The options that are known have various economic and technical limitations. For instance, according to US Patent No. 6,939,443, the use of combinations of polyamide-epichlorohydrin (PAE) resins with anionic polyacrylamide additives with specific charge densities and molecular weights can enhance the dry strength of a paper product. However, these combinations also may elevate the wet strength of the resultant paper to the point that repulping broke paper is extremely difficult and inefficient.

[0003] Polymers of acrylamide or copolymers incorporating acrylamide and a monomer such as diallyldimethylammonium chloride, when treated with a dialdehyde compound such as glyoxal, are widely known to result in resins that can also enhance the dry strength of paper significantly, yet have very limited permanent wet strength properties, allowing the papermaker to easily repulp broke paper. However, these resins also have their limitations. These additives either have a very short shelf-life due to viscosity instability, or are shipped at very low active solids content. Furthermore, when added in the larger amounts, the performance of such dialdehyde-modified acrylamide-containing polymers tends to reach a plateau, making a high-performance product difficult to manufacture.

[0004] Polyvinylamine resins have become popular in the papermaking industry not only because they endow a sheet with increased dry strength, but also because of their easy

handling and application as well as the increased retention and drainage they afford the paper machine. However, when added in ever increasing amounts, they have the negative effect of overflocculating the sheet because of the heavy cationic charge these resins carry.

Overflocculation results in a poorly formed, weaker finished product.

[0005] Other inventions have sought to augment the positive effects of polyvinylamine. According to US Patent No. 6,824,650 and European Patent No. 1,579,071, the combination of polyvinylamine with glyoxalated polyacrylamide resins in a pulp slurry results in enhanced product dry strength. However, the aforementioned drawbacks of glyoxalated polyacrylamides, namely low active solids of the product and limited viscosity stability of the product, are clearly in play.

[0006] US Patent No. 6,132,558 discloses a papermaking system wherein a pulp slurry is treated first with a highly cationic polymer, including vinylamine-containing polymers, of molar mass of 5,000 to 3,000,000 daltons, and subsequently with a second cationic acrylamide-containing polymer of molar mass of more than 4,000,000 daltons, subjected to a shearing stage, then treated with a finely divided inorganic flocculating agent, such as bentonite, colloidal silica, or clay.

[0007] US Patent Publication 2008/0000601 discloses a process of papermaking where the pulp slurry is treated with a polymer, including vinylamine-containing polymers, of molar mass of more than 1,000,000 daltons, as well as a second polymer, including cationic acrylamide-containing polymers, with a molar mass of more than 2,500,000 daltons, all in the absence of finely divided inorganic flocculating agents.

[0008] US Patent No. 6,746,542 discloses a method of papermaking wherein a pulp slurry is treated with starch that has been modified at a temperature above the starch gelatinization temperature with a highly cationic polymer, including vinylamine-containing polymers, of molar mass of less than 1,000,000 daltons. The pulp slurry is subsequently treated with a second polymer, including cationic acrylamide-containing polymers, with a molar mass of more than 1,000,000 daltons.

[0009] US Patent Publication 2008/0196852 discloses a retention aid system for papermaking which comprises at least one polymer, including vinylamine-containing polymers, at least one linear, anionic polymer of molar mass of more than 1,000,000 daltons, and at least one particulate, anionic, crosslinked, organic polymer.

[0010] Combining vinylamine-containing polymers with acrylamide-containing polymers may be both the simplest and most effective means for producing a high performance paper product while maintaining paper machine productivity and repulping broke paper. However, examples from the prior art that may include these polymers have significant drawbacks. For instance, previous examples may require special metering apparatuses, additional steps for treating starch prior to addition to the pulp slurry, or high molar mass polymers that may result in overflocculation of the pulp slurry when added in sufficient amounts to affect dry strength.

BRIEF DESCRIPTION OF THE INVENTION

[0011] Treatment of a pulp slurry with a vinylamine-containing aqueous solution polymer in combination with a cationic or amphoteric acrylamide-containing aqueous solution polymers result in paper with enhanced dry strength.

[0012] This combination is most effective when the active polymer solids content of the acrylamide-containing aqueous solution polymer ranges from 5% to 50% by weight, and the content of the sum of the cationic and anionic monomers in the acrylamide-containing polymer ranges from 5% to 50% on a molar basis of the total monomer content, and the molecular weight of the acrylamide-containing polymer ranges from 75,000 daltons to 1,500,000 daltons.

[0013] The vinylamine-containing polymer is most effective when it contains at least 50% on a molar basis of *N*-vinylformamide monomer, at least 10% of which has been hydrolyzed in the final product and has a molecular weight in the range of from 75,000 daltons to 750,000 daltons. The aqueous solution containing the vinylamine-containing polymer has a total polymer solids content of from 5% to 30% by weight,.

[0014] One embodiment of the invention is a process for the production of paper, board, and cardboard with enhanced dry strength comprising adding to the wet end of a paper machine (a) a vinylamine-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 750,000 daltons and (b) an amphoteric or cationic acrylamide-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 1,500,000 daltons, where the sum of the anionic and cationic monomers comprise at least 5% on a molar basis of the composition of the acrylamide-containing monomer.

[0015] In one embodiment of the process the vinylamine-containing polymer has an *N*-vinylformamide content of at least 50% on a molar basis of the total monomer charged, at least 10% of which has been hydrolyzed in the final polymer, and an active polymer content of from 5% to 30% on a weight basis.

[0016] In one embodiment of the process the acrylamide-containing aqueous solution polymer contains a sum cationic and/or amphoteric monomer charge of from 5% to 50% on a molar basis, and has an active polymer content of from 5% to 50% on a weight basis.

[0017] In one embodiment of the process the acrylamide-containing aqueous solution polymer is of an aqueous dispersion polymer.

[0018] In one embodiment of the process the acrylamide-containing aqueous solution polymer contains a cationic monomer charge of from 5% to 50% on a molar basis, has an active polymer content of from 5% to 50% on a weight basis, and comprises a least one cationic monomer selected from the group consisting of diallyldimethylammonium chloride (DADMAC), 2-(dimethylamino)ethyl acrylate, 2-(dimethylamino)ethyl methacrylate, 2-(diethylaminoethyl) acrylate, 2-(diethylamino)ethyl methacrylate, 3-(dimethylamino)propyl acrylate, 3-(dimethylamino)propyl methacrylate, 3-(diethylamino)propyl acrylate, 3-(diethylamino)propyl methacrylate, *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, *N*-[3-(diethylamino)propyl]acrylamide, *N*-[3-(diethylamino)propyl]methacrylamide, [2-(acryloyloxy)ethyl]trimethylammonium chloride, [2-(methacryloyloxy)ethyl]trimethylammonium chloride, [3-(acryloyloxy)propyl]trimethylammonium chloride, [3-(methacryloyloxy)propyl]trimethylammonium chloride, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride.

[0019] In one embodiment of the process the acrylamide-containing aqueous solution polymer has an overall amphoteric charge.

[0020] In one embodiment of the process the amphoteric acrylamide-containing aqueous solution is comprised of a polyelectrolyte complex consisting of an acrylamide-containing aqueous solution polymer and a cofactor carrying an opposing charge.

[0021] In one embodiment of the process the vinylamine-containing polymer and the acrylamide-containing polymer are a single product blend and the cationic portion of the amphoteric acrylamide-containing polymer is generated by at least one monomer selected from the group consisting of diallyldimethylammonium chloride (DADMAC), *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, *N*-[3-(diethylamino)propyl]acrylamide, *N*-[3-(diethylamino)propyl]methacrylamide, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride.

[0022] In one embodiment of the process the vinylamine-containing polymer and the acrylamide-containing polymer are added to the wet end of a paper machine in a ratio of vinylamine-containing polymer to acrylamide-containing polymer of from 10:1 to 1:50 up to a sum total of 1.25% on a weight basis of the dry pulp, based on the active polymer solids of the polymeric products.

[0023] One embodiment of the invention is the paper product produced by the process of adding to the wet end of a paper machine (a) a vinylamine-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 750,000 daltons and (b) an amphoteric or cationic acrylamide-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 1,500,000 daltons, where the sum of the anionic and cationic monomers comprise at least 5% on a molar basis of the composition of the acrylamide-containing monomer.

[0024] In another embodiment, the invention relates to the method of treating a cellulosic pulp slurry in the wet end of a paper machine with (a) a vinylamine-containing polymer and (b) a cationic or amphoteric acrylamide-containing aqueous solution polymer. It is preferred that the vinylamine-containing polymer is added to the pulp slurry first, followed by the acrylamide-containing polymer.

DETAILED DESCRIPTION OF THE INVENTION

[0025] As used herein, the singular terms "a" and "the" are synonymous and used interchangeably with "one or more" or "at least one" unless the context clearly indicates a contrary meaning. Accordingly, for example, reference to "a compound" herein or in the appended claims can refer to a single compound or more than one compound.

[0026] As used herein and unless otherwise stated, the terms "vinylamine-containing

polymers,” is understood to mean homopolymers of vinylamine (e.g., polyvinylamine or fully hydrolyzed polyvinylformamide), copolymers of vinylamine with other comonomers, partially hydrolyzed polyvinylformamide, partially hydrolyzed vinylformamide copolymers, vinylamine terpolymers, vinylamine homo- and copolymers manufactured by the Hofmann modification of acrylamide polymers, or vinylamine containing polymers that are chemically modified after polymerization. Examples may include those described in US Patent Publication number 2009/0043051 or number 2008/0196851.

[0027] As used herein and unless otherwise stated, the term “acrylamide-containing polymer” refers to the cationic or amphoteric acrylamide-containing aqueous solution polymer.

[0028] As used herein and unless otherwise stated, the term “aqueous solution polymer” refers to a polymer that forms a fully homogenous solution in water when diluted to 1% on a dry solids basis, in the absence of any cosolvent. For instance, an aqueous solution polymer does not include oil-in-water or water-in-oil emulsions. Examples of aqueous solution polymers may include aqueous dispersion polymers, such as are described in US Patents 5,541,252 and 7,323,510 as well as US Patent Publications number 2002/198317 and number 2008/0033094.

[0029] The invention is based in the discovery that the performance of a paper machine and the paper products derived thereby can be greatly enhanced by the treatment of the pulp slurry with a vinylamine-containing polymer in combination with an acrylamide-containing polymer with particular molecular weight and charge attributes as described below. Use of a vinylamine-containing polymer alone provides both strength and drainage performance in the papermaking system; however, when added in ever-increasing amounts, the performance of the paper product first levels off, and then deteriorates, largely due to overfloculation of the forming paper web. It has unexpectedly been found that the addition of vinylamine-containing polymer in conjunction with the addition of aqueous solution acrylamide-containing polymers having substantial amphoteric or cationic charge results in a product with strength performance beyond that which can be attained by using vinylamine-containing or acrylamide-containing polymers alone; moreover, the excellent drainage performance achieved by using a vinylamine-containing polymer can be substantially maintained using such a combination of polymers.

[0030] The vinylamine-containing polymer is most effective when its molecular weight is from 75,000 daltons to 750,000 daltons, more preferably of from 100,000 daltons to 600,000 daltons, most preferably of from 150,000 daltons to 500,000 daltons. The molecular weight can be from 150,000 daltons to 400,000 daltons. Below the molecular weight threshold of 75,000 daltons, little to no strength performance is observed, and substantial drainage performance enhancement is not observed. The vinylamine-containing polymer is not cooked with starch prior to addition to the pulp slurry. A vinylamine-containing polymer above the molecular weight of 750,000 daltons will generally negatively affect formation at dosages required for dry strength enhancement because of the tendency to overfloculate the sheet, resulting in lower strength. An aqueous solution vinylamine-containing polymer above 750,000 daltons either is typically made at such high viscosities as to render product handling extremely difficult, or alternatively is made in such low product polymer solids as to render the product not cost effective to store and ship.

[0031] The active polymer solids percentage of the vinylamine-containing polymer ranges of from 5% to 30%, more preferably from 8% to 20% by weight of the total vinylamine-containing polymer product content. Below 5% active polymer solids, higher molecular weight aqueous solution polymers may be possible, but the product becomes ineffective with respect when shipping and transportation costs are accounted for. On the other hand, as the active polymer solids rises, the molecular weight of the polymer must decrease overall so that the aqueous solution is still easily pumpable. Thus, a practical relationship can be drawn between the total polymer solids of the vinylamine-containing polymer product and the molecular weight of such a polymer, and a correlation can be drawn between these parameters and polymer performance.

[0032] The performance of the vinylamine-containing polymer is influenced by the amount of primary amine present in the product. The vinylamine moiety is typically generated by acidic or basic hydrolysis of *N*-vinylacrylamide groups, such as *N*-vinylformamide, *N*-vinylacetamide, or *N*-vinyl propionamide, most preferably *N*-vinylformamide. The vinylamine-containing polymer is most effective in enhancing the dry strength of a paper product and/or the drainage performance of a papermaking system when the amount of *N*-vinylformamide is at least 50% on a molar basis of the hydrolyzed polymer. After hydrolysis, at least 10% of the *N*-vinylformamide originally incorporated into the resultant polymer should be hydrolyzed. Without wishing to be bound by theory, the hydrolyzed *N*-vinylformamide group may exist in various structures in the final polymer

product such as primary or substituted amine, amidine, guanidine, or amide structures, either in open chain or cyclical forms after hydrolysis.

[0033] The acrylamide-containing polymer is most effective when it contains a substantial amount of a positively charged comonomer(s). Without wishing to be bound by theory, the positively charged monomer allows the acrylamide-containing polymer to adhere to the cellulose fibers due to a charge-charge interaction with negatively charged substances in the pulp slurry, including, but not limited to: pulp fibers, hemicellulose, oxidized starch commonly found in recycled cellulose furnish, anionic strength aids such as carboxymethylcellulose, and anionic trash. The incorporation of cationic groups into the acrylamide-containing polymer is generally not detrimental to the drainage performance of the papermaking system. Without wishing to be bound by theory, the hydrogen-bonding components of the acrylamide-containing polymer, such as amide groups, are effective in enhancing the dry strength of the paper product.

[0034] Suitable comonomers used to impart cationic charge to the polymer include, but are not limited to, diallyldimethylammonium chloride (DADMAC), 2-(dimethylamino)ethyl acrylate, 2-(dimethylamino)ethyl methacrylate, 2-(diethylaminoethyl) acrylate, 2-(diethylamino)ethyl methacrylate, 3-(dimethylamino)propyl acrylate, 3-(dimethylamino)propyl methacrylate, 3-(diethylamino)propyl acrylate, 3-(diethylamino)propyl methacrylate, *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, *N*-[3-(diethylamino)propyl]acrylamide, *N*-[3-(diethylamino)propyl]methacrylamide, [2-(acryloyloxy)ethyl]trimethylammonium chloride, [2-(methacryloyloxy)ethyl]trimethylammonium chloride, [3-(acryloyloxy)propyl]trimethylammonium chloride, [3-(methacryloyloxy)propyl]trimethylammonium chloride, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride. Such cationic monomers can affect the performance of the cationic or amphoteric polymer when incorporated into the polymer backbone.

[0035] The amount of cationic monomer incorporated into a polymer may be from 5% to 50% on a molar basis of all the monomers incorporated into the acrylamide-containing polymer in the case of a cationic polymer. In the case of an amphoteric polymer, the amount of the cationic monomer plus the amount of an anionic monomer described below may be

from 5% to 50%, more preferably from 15% to 40%, on a molar basis of all the monomers incorporated into the acrylamide-containing polymer. The acrylamide-containing polymer may be cross-linked with an agent such as methylene bisacrylamide (MBA) provided the molecular weight and charge guidelines are met as described herein.

[0036] The incorporation of an anionic comonomer into the acrylamide-containing polymer along with the cationic comonomer, forming an amphoteric acrylamide-containing polymer, is also effective in enhancing the dry strength of a paper product made thereby. Without wishing to be bound by theory, the anionic comonomer allows the amphoteric polymer to form a coacervate complex with a wide variety of substances found in a recycled pulp slurry, including, but not limited to: a vinylamine-containing polymer, a cationically charged flocculant or coagulant, cationic or amphoteric starch, polyamidoamine-epichlorohydrin wet strength aids, or another amphoteric acrylamide-containing polymer. Moreover, the combination of cationic and anionic monomers in the acrylamide-containing polymer either enhances or does not negatively affect the drainage performance of a papermaking system when compared to an acrylamide-containing polymer using only an anionic comonomer. Suitable anionic comonomers include, but are not limited to, acrylic acid, methacrylic acid, itaconic acid, itaconic anhydride, maleic anhydride, maleic acid, styrene sulfonate, vinyl sulfonate, 2-acrylamido-2-methylpropane sulfonate (AMPS). Alternatively, such substructures may be generated by hydrolysis of a precursor structure (e.g. generation of methacrylic acid in the polymer backbone *via* hydrolysis of methyl methacrylate after the formal polymerization). The amount of charged monomer incorporated into the acrylamide-containing polymer may affect the performance of the polymer. Such anionic monomers may be used in an amphoteric acrylamide-containing polymer, and the amount of the anionic monomer plus the amount of a cationic monomer described above may be from 5% to 50% on a molar basis of all the monomers incorporated into the acrylamide-containing polymer. The acrylamide-containing polymer may be cross-linked with an agent such as methylene bisacrylamide (MBA) provided the molecular weight and charge guidelines are met as described herein.

[0037] The properties of an amphoteric aqueous solution acrylamide-containing polymer as defined above can also be effectively produced by the use of an acrylamide-containing polyelectrolyte complex. When combined with a vinylamine-containing polymer, such an acrylamide-containing polyelectrolyte complex may also produce benefits similar to those described above when vinylamine-containing polymers are combined with cationic or

amphoteric acrylamide-containing polymers. Although polyelectrolyte complexes in various forms have been disclosed, such as in European Patent Publication No. 1,918,455 A1, herein we disclose the unexpected result that the effectiveness of such polyelectrolyte complexes in generating dry strength beyond what the polyelectrolyte complex may provide on its own, may be achieved when they are used in combination with vinylamine-containing polymers. An acrylamide-containing polyelectrolyte complex contains an acrylamide-containing polymer of either cationic, amphoteric, or anionic charge, as well as a second polymer of a complementary charge. For example, an anionic acrylamide-containing polymer made by polymerization of acrylamide with one of the suitable anionic monomers listed above can form a polyelectrolyte complex with a cationic polymer, which may or may not include acrylamide. Such cationic polymers include, but are not limited to, alkylamine-epichlorohydrin polymers, cationic acrylamide-containing polymers as described above, polyamidoamine-epichlorohydrin polymers, and polyethyleneimine polymers. The acrylamide-containing polyelectrolyte complex may also comprise a cationic acrylamide-containing polymer and an anionic polymer. Such anionic polymers include, but are not limited to, polymers and copolymers of (meth)acrylic acid, polymers and copolymers of maleic acid, and carboxymethyl cellulose. The acrylamide-containing polyelectrolyte complex may be added to the papermaking slurry either as a single blended product or as two separate products, most preferably as a single blended product. The amphoteric polyelectrolyte complex carries a net charge, expressed in milliequivalents per gram (meq/g) of polymer active content. The amphoteric polyelectrolyte complex is generally most stable and useful in combination with vinylamine-containing polymers when the net charge is in the range of from -2 meq/g to +2 meq/g, more preferably of from -1 meq/g to +1 meq/g. The particle size is also an important parameter of the amphoteric polyelectrolyte complex. The complex is most useful when the particle size ranges of from 0.1 microns to 50 microns, more preferably from 0.2 to 5 microns. Other guidelines for active polymer solids, the preferred methods for adding the acrylamide-containing polymer to the pulp slurry, and the ratio of the vinylamine-containing polymer to the acrylamide-containing polymer apply to the total formulation of the acrylamide-containing polyelectrolyte complex, not only the acrylamide-containing polymer portion of the complex.

[0038] The acrylamide-containing aqueous solution polymer, whether it is characteristically a cationic polymer, amphoteric polymer, or amphoteric polyelectrolyte complex as defined above, most effectively enhances the dry strength of a paper product

when its molecular weight is greater than 75,000 daltons. A molecular weight less than 75,000 daltons is not easily retained in the sheet, and above all does not endow paper with significant dry strength properties, although it could be manufactured in such a way as to have a polymer solids content above 50% on a weight basis. However, an acrylamide-containing polymer of greater than 1,500,000 daltons, and especially greater than 2,500,000 daltons may show significant drawbacks. Although at lower dosages, such high molar mass polymers may give good drainage performance, attaining high dry strength typically requires higher dosages of polymers. Such a polymer can significantly overfloculate the sheet when added at a dosage that might significantly impact dry strength, thereby resulting in poor formation and/or poor dry strength. In one embodiment, the molecular weights of the cationic or amphoteric acrylamide-containing aqueous solution polymers can be in the range of from 75,000 to less than 1,500,000 daltons, or can be from 100,000 to less than 1,250,000 daltons, or can be from 100,000 to less than 1,000,000 daltons. Moreover, a polymer of this molecular weight is generally synthesized *via* emulsion or reverse emulsion polymerization, thereby adding significant cost, inconvenience, and environmental and safety risk. For instance, oil or other hydrocarbon, such as mineral oil, is required in the formulation of a reverse emulsion product which adds significant cost to the product but does not by itself add value to the product; significant additional make-down equipment used to store, agitate, dilute, and invert the emulsions; additional chemicals are needed to break or invert the emulsion; and emulsion- or reverse emulsion-type polymers also contain significant amounts of volatile organic compounds, creating a significant health and/or safety hazard. An aqueous solution acrylamide-containing polymer of molecular weight greater than 1,500,000 daltons may in theory be achieved in a product; however, such a product would likely be less than 5% polymer solids, rendering such a product less useful, cost effective, and convenient to a papermaker, or would be made be of such a high viscosity that the product handling would be extremely difficult. Thus, a practical relationship between the total polymer solids and molecular weight generally exists and a general correlation can be drawn between these parameters and polymer performance.

[0039] In one embodiment, the acrylamide-containing polymer is an aqueous dispersion polymer. Acrylamide-containing polymers made by way of aqueous dispersion polymerization of either a cationic or amphoteric nature are of special practical importance when combined with vinylamine-containing polymers. Specific examples are described in US Patent No. 7,323,510 as well as US Patent Publication No. 2008/0033094. These aqueous

solution polymers may have molecular weights of from 300,000 daltons to 1,500,000 daltons, or from 400,000 daltons to less than 1,250,000 daltons, while maintaining polymer solids content of from 10% to 50% on a weight basis. These polymers are of a molecular weight that is somewhat less than traditional flocculants, and are thus less effective than higher molecular weight acrylamide-containing polymers as retention and drainage polymers at low dosage levels, but may generate excellent drainage performance when used at dosage levels adequate for dry strength enhancement without overflocculating a forming cellulosic sheet. Without wishing to be bound by theory, the interaction of vinylamine-containing polymers either with aqueous dispersion acrylamide-containing polymers or with other components of a papermaking system including but not limited to oxidized starch, hemicellulose, or anionic trash, may create especially extensive hydrogen-bonding networks, providing additional dry strength to a paper product without any substantial negative effects on the drainage performance of the papermaking system.

[0040] The vinylamine-containing polymer and the acrylamide-containing polymer may be combined together in a single-product blend. Ratios of the vinylamine-containing polymer to the acrylamide containing polymer range of from 10:1 to 1:50, more preferably in the range of from 5:1 to 1:10, more preferably in the range of from 3:1 to 1:5, most preferably in the range of from 2:1 to 1:4.

[0041] Total amounts of the polymer blend may be added to the pulp slurry in the wet end of the paper machine in amounts of from 0.05% to 1.25% of the weight of dry pulp on a total polymer solids basis. Blends can be made with vinylamine containing polymers and either cationic or amphoteric acrylamide-containing polymers, but most preferably with cationic acrylamide-containing polymers. Without wishing to be bound by theory, anionic components of amphoteric acrylamide-containing polymers may interact in an ionic fashion with cationic components of vinylamine-containing polymers, particularly primary amine groups, to form gels and high viscosity products that are not useful for papermaking. Without wishing to be bound by theory, polymers containing cationic monomers with ester groups, for example, 2-[(acryloyloxy)ethyl]trimethylammonium chloride, can react in aqueous solutions with primary amine groups in the vinylamine-containing polymer to form amide groups, or can hydrolyze to generate the above-mentioned anionic moieties, either of which may form a gelled or prohibitively high viscosity product which is not useful in papermaking. Moreover, the hydrolysis of the relatively expensive cationic acrylate group represents a significant financial loss when considering the cationic acrylamide-containing

polymer. Without wishing to be bound by theory, amide-containing cationic monomers, such as 3-(acrylamidopropyl)trimethylammonium chloride or diallyldimethylammonium chloride (DADMAC) are resistant both to hydrolysis in aqueous solutions as well as reaction with primary amine groups, making them preferred as cationic monomers in the acrylamide-containing polymer to be blended with the vinylamine-containing polymer.

[0042] Vinylamine-containing polymers and acrylamide-containing polymers can be added during the papermaking process in the wet end either in the thick stock, or in the thick stock; either before or after a shear point. The acrylamide-containing polymer may be added first in the wet end of the paper machine, followed by the vinylamine-containing polymer; the acrylamide-containing polymer may be added at the same point separately in the wet end of the paper machine as the vinylamine-containing polymer; the acrylamide-containing polymer may be added at the same point in the wet end of a paper machine as a single product blend; or, more preferably, the vinylamine-containing polymer may be added first in the wet end of the paper machine, followed by the acrylamide-containing polymer. The vinylamine-containing polymer is not reacted with starch prior to addition to the pulp slurry.

[0043] The vinylamine-containing polymer and the acrylamide-containing polymer may be added to the wet end of a paper machine in a ratio of from 1:50 to 10:1 of vinylamine-containing polymer to acrylamide-containing polymer as a ratio of polymer solids; more preferably in a ratio of from 1:10 to 5:1, more preferably in the range of from 1:5 to 3:1, most preferably in the range of from 1:5 to 2:1. Total amounts of the polymer blend may be added to the pulp slurry in the wet end of the paper machine in amounts of 0.05% to 1.25% of the weight of dry pulp on a total polymer solids basis.

[0044] In another embodiment, this invention can be applied to any of the various grades of paper that benefit from enhanced dry strength including but not limited to linerboard, bag, boxboard, copy paper, container board, corrugating medium, file folder, newsprint, paper board, packaging board, printing and writing, tissue, towel, and publication. These paper grades can be comprised of any typical pulp fibers including groundwood, bleached or unbleached Kraft, sulfate, semi-mechanical, mechanical, semi-chemical, and recycled. They may or may not include inorganic fillers.

[0045] The embodiments of the invention are defined in the following Examples. It should be understood that these Examples are given by way of illustration only. Thus various modifications of the present invention in addition to those shown and described herein will be

apparent to those skilled in the art from the foregoing description. Although the invention has been described with reference to particular means, materials and embodiments, it is to be understood that the invention is not limited to the particulars disclosed, and extends to all equivalents within the scope of the appended claims.

EXAMPLES

[0046] Polyvinylamine is abbreviated as PVAm. Size exclusion chromatography (SEC) was used to measure molecular weight. The analysis was accomplished using gel permeation columns (CATSEC 4000 + 1000 + 300 + 100) and Waters 515 series chromatographic equipment with a mixture of 1 % NaNO₃/0.1 % Trifluoroacetic acid in 50:50 H₂O:CH₃CN as the mobile phase. The flow rate was 1.0 mL/min. The detector was a Hewlett Packard 1047A differential refractometer. Column temperature was set at 40 °C and the detector temperature was at 35 °C. The number average (M_n) and weight average molecular weight (M_w) of the polymers were calculated relative to the commercially available narrow molecular weight standard poly(2-vinyl pyridine).

[0047] The net charges or charge densities (Mütek) of the ionized polymers in the present invention were measured at pH 7.0 using a colloid titration method. Charge density (meq/g) is the amount of net charge per unit weight, in milliequivalents per gram of active polymer. The polymer sample is titrated with a titrant of opposing charge. For net cationic polymers, the titrant used is potassium polyvinyl sulfate (PVSK), and for net anionic polymers the titrant used is polydimethyldiallylammonium chloride (DADMAC). The titrant is added until a 0 mV potential is achieved using an autotitrator (Brinkmann Titrino) at a fixed titration rate (0.1 mL/dose, 5 sec) and a Mütek particle charge detector (Model PCD 03, BTG, Mütek Analytic Inc., 2141 Kingston Ct., Marietta, GA, USA) signifying end point detection.

[0048] Linerboard paper was made using a papermaking machine. The paper pulp was a 100 % recycled medium with 50 ppm hardness, 25 ppm alkalinity, 2.5 % GPC D15F oxidized starch (Grain Processing Corp., Muscatine, IA) and 2000 uS/cm conductivity. The system pH was 7.0 unless indicated otherwise, and the pulp freeness was about 380 CSF with the stock temperature at 52 °C. The basis weight was 100 lbs per 3000 ft². Unless otherwise indicated, Stalok 300 cationic starch (Tate & Lyle PLC, London, UK) and PerForm® PC 8713 flocculant (Hercules Incorporated, Wilmington, DE) were added to the wet end of the paper machine in the amount of 0.5% and 0.0125% of dry pulp, respectively. Vinylamine-

containing and acrylamide-containing polymers as described in the above examples were added as dry strength agents to the wet end of the papermaking machine at the indicated levels, expressed as a percentage of weight of polymer active versus dry paper pulp. It is generally accepted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) what a commercial paper machine may use. Ring crush, dry Mullen burst, and dry tensile tests were used to measure the dry strength effects. All dry strength results are expressed as a percentage of the dry strength of paper made without a dry strength resin.

[0049] Drainage efficiency of the various polymeric systems was compared using one of two tests. One test is the Canadian Standard Freeness (CSF) Test. The dose of polymer active varied as is indicated in the tables. The results are summarized in the following tables and the drainage performances of these compositions are expressed as percentage increase over the blank.

[0050] Another method for evaluation of the performance of the drainage process is the vacuum drainage test (VDT). The device setup is similar to the Buchner funnel test as described in various filtration reference books, for example see Perry's Chemical Engineers' Handbook, 7th edition, (McGraw-Hill, New York, 1999) pp. 18-78. The VDT consists of a 300-ml magnetic Gelman filter funnel, a 250-ml graduated cylinder, a quick disconnect, a water trap, and a vacuum pump with a vacuum gauge and regulator. The VDT test was conducted by first setting the vacuum to 10 inches Hg, and placing the funnel properly on the cylinder. Next, 250 g of 0.5 wt. % paper stock was charged into a beaker and then the required additives according to treatment program (e.g., starch, vinylamine-containing polymer, acrylamide-containing polymer, flocculants) were added to the stock under the agitation provided by an overhead mixer. The stock was then poured into the filter funnel and the vacuum pump was turned on while simultaneously starting a stopwatch. The drainage efficacy is reported as the time required to obtain 230 mL of filtrate. The results of the two drainage tests were normalized and expressed as a percentage of the drainage performance observed versus a system that did not include the vinylamine-containing and acrylamide-containing polymers.

[0051] Polymer A is a vinylamine-containing polymer such as Hercobond® 6363 (available from Hercules Incorporated, Wilmington, DE) with a molecular weight in the range of 100,000 daltons to 500,000 daltons with an active polymer solids content of 9% to

15%, an *N*-vinylformamide charge of from 75% to 100%, with a range of hydrolysis from 50% to 100%.

[0052] Polymer B is a vinylamine-containing polymer such as such as Hercobond® 6350 (available from Hercules Incorporated, Wilmington, DE) with a molecular weight in the range of 100,000 daltons to 500,000 daltons with an active polymer solids content of 9% to 15%, an *N*-vinylformamide charge of from 75% to 100%, with a range of hydrolysis from 30% to 75%.

[0053] Polymer C is an amphoteric acrylamide-containing polymer such as Hercobond® 1205 (available from Hercules Incorporated, Wilmington, DE) with a molecular weight in the range of 100,000 daltons to 500,000 daltons with an active polymer solids content of 10% to 25% and a sum total monomer charge of anionic and cationic monomers of from 8% to 20% of the total monomer charge.

[0054] Polymer D is a cationic acrylamide-containing polymer such as Hercobond® 1200 (available from Hercules Incorporated, Wilmington, DE) with a molecular weight in the range of 100,000 daltons to 500,000 daltons, an active polymer solids content of 10% to 25% and a cationic monomer charge of 20% to 40%.

[0055] Comparative Polymer E is an anionic acrylamide-containing polymer such as Hercobond® 2000 (available from Hercules Incorporated, Wilmington, DE) with an anionic monomer charge in the range of from 5% to 20%.

[0056] Polymer F and Polymer G are cationic acrylamide-containing aqueous dispersion polymers such as Praestaret® K325 and K350, respectively (available from Ashland Inc., Covington, KY) with a molecular weight in the range of 500,000 daltons to 1,500,000 daltons, an active polymer solids content of 20% to 45% and a cationic monomer charge of 10% to 40%.

[0057] Polymer H is an amphoteric acrylamide-containing polyelectrolyte complex such as Hercobond® 1822 (available from Hercules Incorporated, Wilmington, DE) with a molecular weight in the range of 100,000 daltons to 500,000 daltons with an active polymer solids content of 10% to 25%, and a net charge of from -2 meq/g to +2 meq/g.

[0058] Polymer K is a cationic acrylamide-containing polymer such as Praestamin® CL (available from Ashland Inc., Covington, KY) with a molecular weight in the range of

100,000 daltons to 400,000 daltons with an active polymer solids content of 15% to 30%. The cationic comonomer in Polymer K is 3-(acrylamidopropyl)trimethylammonium chloride. Polymer K can be blended with vinylamine-containing polymers such as Polymer A and Polymer B to form a single product.

EXAMPLE 1

[0059] Table 1 shows the results of a pilot paper machine trial using Polymer A, amphoteric Polymer C, and cationic Polymer D. The pH of the system was adjusted to 6.5. Alum (Croydon, PA) and HipHase 35 rosin size (Hercules, Inc., Wilmington, DE) were used in the amount of 0.5% and 0.3% of dry pulp, respectively. OptiPlus 1030 amphoteric starch (National Starch, Bridgewater, NJ) was added in the place of Stalok 300 cationic starch, still used at 0.5% of dry pulp.

Table 1. Strength and drainage properties of paper made with Polymer A and an acrylamide containing polymer.

Entry	Additive 1	%	Additive 2	%	Dry Tensile	Dry Mullen Burst	Ring Crush	Drainage
1	--	--	--	--	100	100	100	100
2	Polymer A	0.050	--	--	102.4	106.2	105.7	110
3	Polymer A	0.125	--	--	103.2	110.2	108.7	131
4	--	--	Polymer C	0.100	104.5	105.7	104.8	107
5	--	--	Polymer C	0.250	103.8	113.0	110.1	110
6	Polymer A	0.050	Polymer C	0.100	102.8	108.0	110.4	121
7	Polymer A	0.125	Polymer C	0.100	112.8	116.8	112.6	142
8	Polymer A	0.088	Polymer C	0.175	106.5	112.7	117.8	137
9	Polymer A	0.050	Polymer C	0.250	110.4	109.2	114.2	121
10	Polymer A	0.125	Polymer C	0.250	108.9	121.0	116.9	153
11	--	--	Polymer D	0.100	103.2	93.1	104.6	129
12	--	--	Polymer D	0.250	106.5	106.2	109.9	150
13	Polymer A	0.050	Polymer D	0.100	103.2	98.2	107.0	137
14	Polymer A	0.125	Polymer D	0.100	105.1	108.3	111.4	137
15	Polymer A	0.088	Polymer D	0.175	107.7	113.0	110.9	150
16	Polymer A	0.050	Polymer D	0.250	104.6	107.7	109.5	142
17	Polymer A	0.125	Polymer D	0.250	106.8	117.4	107.2	147

[0060] Table 1 shows that strength could be markedly improved by addition of the acrylamide-containing polymer, and that drainage performance was maintained if not improved by adding more of the acrylamide-containing polymer. It is noted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 2

[0061] Table 2 shows the drainage performance of three different acrylamide-containing polymer additives using the same whitewater and pulp as indicated in the strength testing illustrated in Table 1. The drainage performance was evaluated using the CSF test as indicated above. Entries 18 to 23 are shown for comparison.

Table 2 Drainage properties of pulp made using various acrylamide-containing polymers with Polymer A.

Entry	Additive 1	% of dry pulp	Additive 2	% of dry pulp	% of drainage
1	--	--	--	--	100
2	Polymer A	0.050	--	--	110
3	Polymer A	0.125	--	--	131
4	--	--	Polymer C	0.100	107
5	--	--	Polymer C	0.250	110
6	Polymer A	0.050	Polymer C	0.100	121
7	Polymer A	0.125	Polymer C	0.100	142
8	Polymer A	0.088	Polymer C	0.175	137
9	Polymer A	0.050	Polymer C	0.250	121
10	Polymer A	0.125	Polymer C	0.250	153
11	--	--	Polymer D	0.100	129
12	--	--	Polymer D	0.250	150
13	Polymer A	0.050	Polymer D	0.100	137
14	Polymer A	0.125	Polymer D	0.100	137
15	Polymer A	0.088	Polymer D	0.175	150
16	Polymer A	0.050	Polymer D	0.250	142
17	Polymer A	0.125	Polymer D	0.250	147

18	--	--	Comparative Polymer E	0.100	96
19	--	--	Comparative Polymer E	0.250	94
20	Polymer A	0.050	Comparative Polymer E	0.100	110
21	Polymer A	0.125	Comparative Polymer E	0.100	134
22	Polymer A	0.088	Comparative Polymer E	0.175	118
23	Polymer A	0.050	Comparative Polymer E	0.250	104
24	Polymer A	0.125	Comparative Polymer E	0.250	134

[0062] Table 2 demonstrates that the drainage performance of the pulp slurry is weaker when the anionic acrylamide-containing polymer (Comparative Polymer E) is used compared to the amphoteric and cationic acrylamide-containing polymers (Polymer C and Polymer D). It is noted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 3

[0063] Table 3 shows results of a pilot paper machine trial using a vinylamine-containing polymer and a cationic acrylamide containing polymer. In this example, as in all following examples, the pH was maintained at 7.0, no alum was included in the furnish, and no sizing agents were employed.

Table 3. Results of pilot paper machine trial at pH 7.0 and in the presence of Polymer B and cationic acrylamide-containing Polymer D.

Entry	Additive 1	%	Additive 2	%	Dry Tensile	Dry Mullen Burst	Ring Crush	Drainage
1	--	--	--	--	100	100	100	100
2	Polymer B	0.100	--	--	96.3	95.7	100.9	98
3	Polymer B	0.300	--	--	102.5	104.0	112.4	137
4	--	--	Polymer D	0.100	104.5	108.6	107.1	109
5	--	--	Polymer D	0.300	105.7	107.4	106.0	115
6	Polymer B	0.100	Polymer D	0.100	100.8	95.2	105.6	134
7	Polymer B	0.300	Polymer D	0.100	110.1	109.9	116.6	120
8	Polymer B	0.200	Polymer D	0.200	112.9	115.8	119.9	118
9	Polymer B	0.100	Polymer D	0.300	115.7	123.0	113.7	115
10	Polymer B	0.300	Polymer D	0.300	110.4	120.2	111.3	112

[0064] Table 3 demonstrates that high dosages of the two polymers, excellent strength performance can be achieved when the two chemicals were added together compared to their performance alone. This method allows the papermaker to achieve greater efficiency in chemical use, and the added strength achieved when the two chemicals are added together allows the papermaker to reduce the usage of the expensive vinylamine-containing Polymer B. It is noted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 4

[0065] Table 4 shows a pilot paper machine trial employing an amphoteric acrylamide-containing polymer in combination with the vinylamine-containing polymer. This trial was performed under conditions similar to Example 3 above. However, in this case, the amphoteric acrylamide-containing Polymer C was used, rather than the cationic acrylamide-containing Polymer D.

Table 4. Results of pilot paper machine trial with Polymer B and amphoteric acrylamide-containing Polymer C.

Entry	Additive 1	%	Additive 2	%	Dry Tensile	Dry Mullen Burst	Ring Crush	Drainage
1	--	--	--	--	100	100	100.0	100
2	Polymer B	0.100	--	--	98.9	104.7	102.2	105
3	Polymer B	0.300	--	--	104.3	123.5	108.0	143
4	--	--	Polymer C	0.100	100.4	103.0	102.4	102
5	--	--	Polymer C	0.300	100.9	101.9	103.9	109
6	Polymer B	0.100	Polymer C	0.100	102.1	108.1	104.1	95
7	Polymer B	0.300	Polymer C	0.100	101.2	116.4	110.7	142
8	Polymer B	0.200	Polymer C	0.200	103.3	112.3	109.8	119
9	Polymer B	0.100	Polymer C	0.300	103.0	112.8	105.3	105
10	Polymer B	0.300	Polymer C	0.300	106	107.9	117.4	131

[0066] Table 4 shows that Mullen Burst and Ring Crush can be especially enhanced with the treatment with the two polymers in tandem versus the polymers in isolation. The drainage performance was affected only marginally. It is noted that the dosages typically

used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 5.

[0067] Table 5 shows the effect of combining aqueous dispersion polymers with the vinylamine-containing Polymer B.

Table 5. Addition of aqueous dispersion Polymers F and G to Polymer B to achieve enhanced strength

Entry	Additive 1	%	Additive 2	%	Dry Tensile	Dry Mullen Burst	Ring Crush	Drainage
1	--	--	--	--	100	100	100	100
2	Polymer B	0.100	--	--	99.0	107.6	105.4	117
3	Polymer B	0.300	--	--	101.8	109.8	107.7	138
4	--	--	Polymer F	0.100	101.0	105.3	104.0	124
5	--	--	Polymer F	0.300	102.8	102.4	110.6	155
6	Polymer B	0.100	Polymer F	0.100	97.5	104.6	104.1	136
7	Polymer B	0.300	Polymer F	0.100	104.2	111.8	111.0	135
8	Polymer B	0.200	Polymer F	0.200	104.1	116.9	110.7	140
9	Polymer B	0.100	Polymer F	0.300	105.5	110.4	109.1	157
10	Polymer B	0.300	Polymer F	0.300	108.3	119.2	114.6	125
11	--	--	Polymer G	0.100	98.6	98.4	102.2	123
12	--	--	Polymer G	0.300	99.5	102.3	101.2	151
13	Polymer B	0.100	Polymer G	0.100	101.1	101.0	106.7	134
14	Polymer B	0.300	Polymer G	0.100	104.9	118.5	108.9	142
15	Polymer B	0.200	Polymer G	0.200	103.6	114.8	110.2	145
16	Polymer B	0.100	Polymer G	0.300	105.4	109.7	106.7	153
17	Polymer B	0.300	Polymer G	0.300	107.2	130.0	111.7	139

[0068] Table 5 demonstrates that drainage can be maintained while achieving significantly enhanced levels of dry strength with aqueous dispersion polymers. It is noted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength

polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 6

[0069] Table 6 shows the combination of vinylamine-containing Polymer B with an amphoteric acrylamide-containing polyelectrolyte complex Polymer H.

Table 6. Pilot paper machine trial using an amphoteric acrylamide-containing polyelectrolyte complex Polymer H with Polymer B.

Entry	Polymer B added (%)	Polymer H added (%)	Dry Tensile	Dry Mullen Burst	Ring Crush
1	0.0	0.0	100	100	100
2	0.0	0.2	99.9	100.8	100.6
3	0.0	0.4	101.1	104.0	102.9
4	0.0	0.6	98.2	103.6	101.5
5	0.1	0.0	93.2	97.7	97.0
6	0.1	0.2	96.6	93.8	100.9
7	0.1	0.4	102.4	102.9	100.9
8	0.1	0.6	102.0	103.5	102.3
9	0.2	0.0	96.6	97.8	101.4
10	0.2	0.2	101.8	107.3	109.1
11	0.2	0.4	109.2	109.5	110.8
12	0.2	0.6	110.4	114.4	112.4
13	0.3	0.0	97.5	102.4	105.3
14	0.3	0.2	107.4	116.0	112.6
15	0.3	0.4	115.6	122.1	115.1
16	0.3	0.6	114.7	121.6	116.2

[0070] Table 6 shows that results comparable to amphoteric acrylamide-containing polymers can be achieved by using the amphoteric acrylamide containing polyelectrolyte complex. Excellent dry strength levels were achieved, at additive levels at which performance typically begins to level off. It is noted that the dosages typically used for dry strength polymers on the pilot paper machine are much greater (i.e. at least double) than what is comparably effective on a commercial paper machine. For example if 0.10 % of additive is an effective amount for a dry strength polymer on the pilot paper machine then the effective amount on the commercial machine would be about 0.05% or less.

EXAMPLE 7

[0071] Table 7 shows dry strength and drainage testing results using a single product blend of Polymer K and Polymer B. Regardless of the ratio of the two polymers in the blend, the additive was used at a dosage level of 0.3% versus the dry pulp.

Table 7. Use of a single-product blend of Polymer K and B to achieve enhanced dry strength

Entry	Polymer K: Polymer B	Active solids (%)	Dry Tensile	Dry Mullen Burst	Ring Crush	Wet Tensile	Drainage
1	0:4	12.7	101.9	105.5	108.6	373.7	159.6
2	1:3	14.6	105.7	110.7	109.4	347.9	149.0
3	1:1	17.2	107.9	108.7	108.0	297.5	127.2
4	3:1	20.8	108.2	108.8	109.7	200.9	109.0

[0072] Table 7 illustrates that using a single product blend of a vinylamine-containing polymer and a cationic acrylamide-containing polymer, improved dry strength results can be obtained in the dry tensile and dry mullen burst categories while offering comparable ring crush results. The single product blend is especially useful in that it offers the papermaker the ease of adding a single product to the paper machine, but the different blend ratios make it possible to tune the product to the papermaker's needs. For instance, if lower wet strength is needed to reduce repulping energy, a single product blend can be made to meet that need while maintaining or improving dry strength properties. Or, if the paper machine is already running near its maximum speed, the amount of drainage the product provides can be matched to the papermaker's need without compromising dry strength. Furthermore, the single product blend can have a significantly higher active solids content without negatively impacting dry strength, thus reducing ecological impact due to transportation of low solids content freight to the paper mill.

CLAIMS

1. A process for the production of paper, board, and cardboard with enhanced dry strength comprising adding to the wet end of a paper machine (a) a vinylamine-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 750,000 daltons and (b) an amphoteric or cationic acrylamide-containing aqueous solution polymer having a molecular weight of from 75,000 daltons to 1,500,000 daltons, wherein the sum of the anionic and cationic monomers comprises at least 5% on a molar basis of the composition of the acrylamide-containing monomer.
2. The process according to claim 1 wherein the active polymer content of the vinylamine containing aqueous solution polymer is from 5% to 30% on a dry weight basis and wherein the vinylamine-containing polymer has an *N*-vinylformamide content of at least 50% on a molar basis of the total monomer charged prior to hydrolysis, and at least 10% of the *N*-vinylformamide has been hydrolyzed in the final polymer..
3. The process according to claim 1 wherein the vinylamine-containing polymer has a molecular weight of from 150,000 daltons to 500,000 daltons.
4. The process according to claim 1 wherein the acrylamide-containing aqueous solution polymer contains a sum cationic and/or amphoteric monomer charge of from 5% to 50% on a molar basis, and has an active polymer content of from 5% to 50% on a weight basis.
5. The process according to claim 1 wherein the acrylamide-containing aqueous solution polymer is cationic and has a molecular weight of from 75,000 daltons to 750,000 daltons.
6. The process according to claim 1 wherein the acrylamide-containing aqueous solution polymer is an aqueous dispersion polymer.
7. The process according to claim 6 wherein the acrylamide-containing aqueous solution polymer is an aqueous dispersion polymer having a molecular weight of from 300,000 daltons to 1,500,000 daltons.

8. The process according to claim 6 wherein the acrylamide-containing aqueous solution polymer is an aqueous dispersion polymer having a molecular weight of from 400,000 daltons to less than 1,250,000 daltons.
9. The process according to claim 1, wherein the acrylamide-containing aqueous solution polymer contains a cationic monomer charge of from 5% to 50% on a molar basis, has an active polymer content of from 5% to 50% on a weight basis, and comprises a least one cationic monomer selected from the group consisting of : diallyldimethylammonium chloride (DADMAC), 2-(dimethylamino)ethyl acrylate, 2-(dimethylamino)ethyl methacrylate, 2-(diethylaminoethyl) acrylate, 2-(diethylamino)ethyl methacrylate, 3-(dimethylamino)propyl acrylate, 3-(dimethylamino)propyl methacrylate, 3-(diethylamino)propyl acrylate, 3-(diethylamino)propyl methacrylate, *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, *N*-[3-(diethylamino)propyl]acrylamide, *N*-[3-(diethylamino)propyl]methacrylamide, [2-(acryloyloxy)ethyl]trimethylammonium chloride, [2-(methacryloyloxy)ethyl]trimethylammonium chloride, [3-(acryloyloxy)propyl]trimethylammonium chloride, [3-(methacryloyloxy)propyl]trimethylammonium chloride, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride.
10. The process according to claim 4, wherein the acrylamide-containing aqueous solution polymer has an overall amphoteric charge.
11. The process according to claim 10 wherein the acrylamide-containing aqueous solution polymer is amphoteric and has a molecular weight of from 75,000 daltons to 750,000 daltons.
12. The process according to claim 10, wherein the amphoteric acrylamide-containing aqueous solution is comprised of a polyelectrolyte complex consisting of an acrylamide-containing aqueous solution polymer and a cofactor carrying a complementary charge.

13. The process according to claim 12, wherein the amphoteric acrylamide-containing aqueous solution is comprised of a polyelectrolyte complex having a molecular weight of from 100,000 daltons to less than 1,000,000 daltons.
14. The process according to claim 1, wherein the vinylamine-containing polymer and the acrylamide-containing polymer are added to the papermachine as a single product blend.
15. The process according to claim 14, wherein the cationic portion of the acrylamide-containing polymer is generated by at least one monomer selected from the group consisting of diallyldimethylammonium chloride (DADMAC), *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, *N*-[3-(diethylamino)propyl]acrylamide, *N*-[3-(diethylamino)propyl]methacrylamide, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride.
16. The process according to claim 15, wherein the cationic portion of the acrylamide-containing polymer is generated by at least one monomer selected from the group consisting of diallyldimethylammonium chloride (DADMAC), *N*-[3-(dimethylamino)propyl]acrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide, 3-(acrylamidopropyl)trimethylammonium chloride, and 3-(methacrylamidopropyl)trimethylammonium chloride.
17. The process according to claim 1, wherein the vinylamine-containing polymer and the acrylamide-containing polymer are added to the wet end of a paper machine in a ratio of vinylamine-containing polymer to acrylamide-containing polymer of from 10:1 to 1:50 up to a sum total of 1.25% on a weight basis of the dry pulp, based on the active polymer solids of the polymeric products.
18. A paper product produced by the process of claim 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/061750

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H21/18
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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/136756 A2 (HERCULES INC [US]) 29 November 2007 (2007-11-29) paragraphs [0027], [0028], [0032]; claims 1-23 -----	1,3,5, 9-11, 14-16,18
X	US 6 824 650 B2 (LINDSAY JEFF [US] ET AL) 30 November 2004 (2004-11-30) cited in the application paragraph [0119]; claims 1-26 -----	1,9,18
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document 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>	<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>
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Date of the actual completion of the international search 31 May 2011	Date of mailing of the international search report 14/06/2011
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 Karlsson, Lennart

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/061750

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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