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(54) Title: ANIONIC-CATIONIC POLYMER BLEND FOR SURFACE SIZE

(57) Abstract: A composition for surface sizing and strengthening of paper and other cellulosic products and the related sizing method and resulting sized product, wherein the composition is an aqueous mixture of a film-forming binder, such as starch and an anionic polymer and a cationic polymer.



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ANIONIC-CATIONIC POLYMER BLEND FOR SURFACE SIZE

FIELD OF THE INVENTION

- [01] The present invention relates to a surface size composition for cellulosic products, such as paper. The composition also improves paper surface strength. In particular, the invention relates to a surface size composition comprising a mixture of film-forming binder, such as starch, and a blend of an anionic polymer and a cationic polymer.

DESCRIPTION OF RELATED ART

- [02] Paper and other cellulosic products often are sized, i.e., are treated with a composition in order to improve those characteristics of the paper important for printing, such as surface porosity and hydrophobicity. Sizing typically influences absorption by the substrate of water, water-borne compositions, and inks. This effect, in turn, generates higher ink penetration time values, reduced lateral spread of printing inks, as well as improved imaging and contrast with various printing technologies. Thus, hydrophobic surface size agents improve printability primarily by decreasing paper sheet absorbency and enhancing surface resistance to liquid (ink) penetration.
- [03] There are two principal ways for sizing paper, internal sizing (also known as bulk sizing) and surface sizing. Internal sizing involves mixing a sizing agent or composition with the aqueous suspension of paper pulp at the wet-end of a paper machine and then forming a sheet, or web, having a uniform distribution of sizing agent and pulp. Most of the internal sizing agents are small molecules (AKD, ASA, rosin, etc.). Surface sizing involves applying the sizing agent to the surface of a previously formed web. Surface sizing typically increases the hydrophobic character, improves product quality and is less expensive than internal sizing because almost the entire sizing agent is retained on the surface of the treated paper product. Most of the surface-sizing agents are macromolecular compounds.

- [04] A variety of natural and synthetic resins have been used as surface sizing agents. Surface sizing agents may be anionic, cationic, or amphoteric, and may be used in combination with other agents of the same electrical charge type. The effectiveness of a particular sizing agent is influenced by the hydrophilic-hydrophobic balance in its molecule. Illustrative of such known sizing agents are modified starches, modified petroleum resins, and synthetic copolymers, such as copolymers of an ethylenically unsaturated monomer with an acrylate, styrene-maleic anhydride (SMA) copolymers, and the like. In sizing compositions made from such materials, the surface-sizing agent is dissolved or dispersed in water.
- [05] Exemplary of the prior art of surface sizing agents can be mentioned the following issued U.S. Patents: 3,941,736; 4,109,053; 4,112,155; 4,115,331; 4,835,212; 4,855,343; 5,139,614; 5,258,466; 5,290,849; 5,525,661; 5,591,489; 5,795,932; 5,824,190; 6,051,107; 6,087,457; 6,114,417; 6,171,444; 6,284,099 and 6,310,132.
- [06] The performance of many of these known sizing agents often is not entirely satisfactory for certain applications. Various printing technologies continue to require paper surfaces with high integrity and resistance to the abrasive effects of the printing processes. Fiber picking, linting and filler dusting all contribute to decreased runnability of paper in various printing processes. The accumulation of lint degrades the quality of the print job and lowers productivity as more frequent cleaning is required. Thus, there exists a need for surface sizing agents that overcome or ameliorate these surface defects. In particular, regardless of their ability to reduce surface absorption, often measured by the Hercules Sizing Test (HST), almost all sizing agents show relatively high values for the Adams Wet Rub test. For paper to be used in offset printing applications especially, a satisfactory (*i.e.*, lower) result in the Adams Wet Rub test is important.
- [07] Thus, there remains a need in the art for new surface sizing compositions that are easily prepared and easy to use, particularly size compositions that can be used both in the acidic pH range, in the case of alum-containing papers, and in the neutral to weakly alkaline pH range in the case of alum-free and chalk-containing papers and which give an outstanding sizing effect.

- [08] United States Patent Application 20020100567 describes a process for internally sizing paper comprising adding to an aqueous suspension of paper fibers, and optional fillers, an anionic or cationic sizing dispersion of AKD, and a sizing promoter comprising a cationic organic polymer having an aromatic group; and an anionic polymer having an aromatic group selected from step-growth polymers, polysaccharides and naturally occurring aromatic polymers, wherein the sizing dispersion and sizing promoter are added separately to the aqueous suspension.
- [09] Dasgupta U.S. 5,338,407 describes a process for enhancing the dry strength of paper without reducing its softness, in which a mixture of an anionic carboxymethyl guar or a carboxymethyl hydroxyethyl guar and a cationic guar, which may be prepared by reacting a natural guar with caustic and subsequently with quaternary ammonium chloride, is added to a bleached pulp furnish (wet end).
- [10] Allen et al., U.S. 6,294,645 describes a composition useful for imparting dry-strength to paper without substantially increasing the paper's wet-strength wherein the resin system comprises a cationic component and an anionic component. The cationic component comprises a reaction product of an intralinker and a polyamidoamine. The anionic component comprises an anionic component consisting of copolymers of acrylamide and at least one member selected from the group consisting of acrylic acid, itaconic acid, methacrylic acid and 2-acrylamido-2-methyl-1-propanesulfonic acid and salts thereof. Alternatively, the anionic component comprises an anionic component selected from the group consisting of carboxymethylcellulose, carboxymethyl guar, alginic acid, pectin, poly(2-acrylamido-2-methyl-1-propanesulfonic acid), and salts thereof. Preferably, the salts of the anionic component are the sodium salts thereof. The composition is added at the wet end of a paper machine.

BRIEF DESCRIPTION OF THE INVENTION

- [11] The present invention is directed to a composition of matter for surface sizing of paper and other cellulosic products and to the related surface sizing method and to the sized substrate. The composition according to the present invention will

provide size and impart surface strength to cellulosic substrates such as paper. In particular, the surface sizing composition of the present invention is a mixture of a film-forming binder, such as starch, and an anionic polymer and a cationic polymer.

- [12] The present invention is directed to imparting surface size and surface strength via surface application to cellulosic substrates and should be distinguished from compositions and processes for internally sizing and strengthening paper.

DETAILED DESCRIPTION OF THE INVENTION

- [13] The invention is directed to a composition of matter for surface sizing and strengthening paper and other cellulosic products, to the related process of surface sizing and to the resulting product. The composition is a mixture of an anionic polymer and a cationic polymer with a film-forming binder such as starch.
- [14] The term "polymer" is used throughout this application in its conventional sense to refer to compounds having about ten or more monomer units, and is intended to include homopolymers as well as copolymers. The term "monomer" is used herein to refer to compounds that are not polymeric.
- [15] Paper sized with the composition of the present invention will typically exhibit acceptable resistance to penetration of ink and aqueous liquids, adequate surface smoothness and surprisingly improved surface strength, such that linting is reduced.
- [16] As noted above, a key feature of the present invention resides in the discovery that by combining an anionic polymeric sizing agent with a cationic polymeric sizing agent in the presence of a film-forming binder, especially starch, one obtains a surface sizing composition that results in a sized cellulosic product having satisfactory surface absorbance performance, while exhibiting surprisingly improved surface strength as indicated by the Adams Wet Rub test. While not wishing to be bound by any theory of operation, applicants believe that the surface strength improvement flows from the interaction of the anionic and cationic components on the paper surface to provide a reinforced crosslinked layer.

- [17] As used herein, "crosslinked" and similar terms are intended to embrace the structural and/or morphological change that occurs, for example, by covalent chemical reaction, ionic interaction or clustering, improved adhesion to the substrate, phase transformation or inversion, and hydrogen bonding, in the sizing composition of the present invention as it is dried and set to modify the surface properties (size and strength) of a flexible, porous cellulosic substrate, such as paper, to which an effective amount of the sizing composition has been applied.
- [18] Suitable anionic polymers for use in the composition as the anionic polymeric agent of the invention include hydrolyzed copolymers of maleic anhydride with another unsaturated comonomer such as styrene, as well as salts (e.g., ammonium, potassium or sodium salts) of such copolymers. The anionic (co)-polymer can be in a solution or in a dispersion.
- [19] Also included within the group of anionic polymers suitable for use in the present invention are the other well known, alkali soluble, acid-containing copolymers. Examples of such alkali soluble, acid containing copolymers useful in this invention are: styrene-acrylic acid (SAA) copolymers, styrene-methacrylic acid copolymers, styrene-acrylonitrile-acrylic acid copolymers, styrene-butyl acrylate-acrylic acid copolymers, acrylamide-acrylic acid copolymers and the like. Instead of styrene, other hydrophobic monomers may be contained in the acid containing copolymers, such as alpha-methylstyrene; alkyl substituted styrenes, such as vinyl toluene; acrylonitrile; vinyl chloride, acrylic- and (meth)acrylic esters, such as butyl acrylate, methyl methacrylate; or the like, or mixtures thereof; vinyl esters, such as vinyl acetate or vinyl laurate; fumarate esters, such as dibutyl fumarate; maleate esters, such as dibutyl maleate; itaconate esters, such as dibutyl itaconate; olefins, such as ethylene, and the like, or mixtures thereof.
- [20] In addition, instead of acrylic- or methacrylic acid, other copolymerizable, unsaturated acids also may be used in the alkali soluble, acid-containing copolymers. Examples are: maleic acid, fumaric acid, crotonic acid; itaconic acid; monoalkyl maleates, such as monoethyl maleate; aconitic acid; and the like. Unsaturated sulfonic acids, such as vinyl sulfonic acid or styrene sulfonic acid and the like may also be used. The weight average molecular weight of the alkali

soluble, acid-containing copolymer is generally from 3,000 to 1,000,000, preferably from about 10,000 to 150,000 Mw (weight average molecular weight). Again, these copolymers can be used as their salts, such as their ammonium salts.

[21] One specific anionic polymeric agent is a solubilized styrene-maleic acid (also referred to as "SMA") copolymer. The styrene/maleic acid copolymer may comprise 50-80 weight % styrene and 50-20 weight % maleic acid and may have a molecular weight of between about 3,000 and about 300,000. This copolymer can be solubilized by forming its ammonium salt in any manner known to the skilled practitioner. Such anionic copolymers are commercially available from G-P Resins, Inc. under the trade name NovaCote® 1936 and NovaCote® 2000. A suitable anionic compound also might be a polymeric latex having sulfonic or carboxylic moieties such as NovaCote® 1934, also available from G-P Resins, Inc. Also commercially available is another G-P product suitable for use as the anionic polymer, Ambond 1500, which is an acrylamide-acrylic acid copolymer grafted on starch. One advantage of using such a material in the preparation of the sizing composition of the present invention is that a single component provides the composition with both the required anionic agent as well as the film-forming binder component, described below in more detail. Finally, a hybrid anionic component such as an ammonium SMA solution and a styrene-acrylate copolymer (SAE) dispersion, available from G-P Resins, Inc. as NovaCote® PS2, or an anionic guar gum such as a carboxymethyl guar, obtained by reacting a natural guar with caustic and then with monochloroacetate, can also be used as the anionic polymer.

[22] Examples of suitable cationic polymers useful as the cationic polymeric agent include polyamines, polyethylene imines, polyamidoamine-epichlorohydrin resins (such as AMRES 25HP available from G-P Resins, Inc.), dialkylamine-epichlorohydrin resins, homo- and copolymers based on monomers selected from diallyldimethyl-ammonium chloride, vinyl amines, (meth)acrylamides and (meth)acrylates. The use of the term (meth)acrylamide and similar terms is a shorthand notation meant to embrace both acrylamide and methacrylamide. The cationic monomers can be acid addition salts and/or quaternary ammonium salts.

Examples of suitable (meth)acrylamides and (meth)acrylates include dialkylaminoalkyl (meth) acrylamides and dialkylaminoalkyl (meth)acrylates, preferably their quaternary ammonium salts. The molecular weight of the cationic polymer may depend on the type of polymer and its charge density. Suitably the molecular weight is below 1,000,000 and preferably below 600,000. The lower molecular weight limit is usually 2,000 and preferably about 5,000.

- [23] One suitable cationic polymer can be prepared by polymerizing a cationic monomer such as a diallyl quaternary monomer (generally diallyl dimethyl ammonium chloride, DADMAC); but may also be a dialkylaminoalkyl (meth) - acrylate or -acrylamide wherein the alkyl and alkylene groups are usually C₁₋₃, generally as an acid addition or quaternary ammonium salt, possibly with a small amount of acrylamide. For instance it may be dimethylaminoethyl acrylate or methacrylate usually as a quaternary ammonium salt or dimethylaminopropyl--acrylamide or -methacrylamide, again generally as quaternary salt. The quaternizing group is usually methyl chloride or another aliphatic group. In such polymers, the amount of cationic monomer can be from 5 to 45% and the amount of acrylamide can be from 95 to 55%. If desired small amounts of other ethylenically unsaturated monomers can be included in the monomer blend but this is usually unnecessary and the polymer conveniently is formed from the binary blend. Cationic homopolymers of water soluble ethylenically unsaturated cationic monomer optionally with a comonomer, preferably not more than 90% by weight acrylamide, are generally suitable. The ethylenically unsaturated cationic monomers can be any of those cationic monomers discussed above but the monomer is preferably diallyl dimethyl ammonium chloride (DADMAC). Generally it is a homopolymer or a copolymer of at least 5 and usually at least 10% DA DMAC with the balance being acrylamide.

- [24] Another class of cationic polymers that can be used as the cationic polymeric agent are the co-polyhydroxyaminoethers of bis-phenol (BLOX[®] product type available from Dow). Again, the polymers can be provided as their acid addition salts and/or quaternary ammonium salts. Also suitable are hydroxyethyl acrylate-co-2-methacryloyloxyethyl dimethyl ammonium chloride and a cationic guar

prepared by reacting natural guar with caustic and then with a quaternary ammonium chloride.

- [25] One particularly useful cationic polymer is a DADMAC-acrylamide copolymer grafted on starch (Ambond 1520). Such grafted starch polymers are prepared by the graft polymerization of the acrylamide vinyl monomer on to a starch substrate. As is well known in the art, there are various free radical polymerization methods useful for grafting vinyl monomers to starch, e.g., radiation, redox-based free radical polymerization and mechanical fission. One particularly preferred method involves preparing a solution of the starch and acrylamide, adding thereto an appropriate free radical catalyst, and then carrying out the polymerization below the pasting temperature of the starch. Typical free radical catalysts that may be used are hydrogen peroxide, solution soluble organic peroxides and hydroperoxides, and persulfates. An activator, which is typically a mild reducing agent can also be added along with the catalyst. All of these methods are well-known to those skilled in the art and require no further discussion herein.
- [26] Styrene-maleic anhydride copolymers in imide form (3-propyl-dimethyl ammonium chloride) are also suitable as a cationic surface size. They may also provide a surface strength in conjunction with an anionic water-soluble or water dispersible polymer. The styrene content ranges between 50% and 80% based on weight. The imide SMA can be dissolved in acetic acid or in hydrochloric acid solutions.
- [27] A cationic surface size also can be a cationic latex obtained by emulsion copolymerization of styrene with butyl acrylate and having cationic charges on the particle surface. The styrene content may range from 30% to 75% and the cationic charge is anywhere between 0.2-1.0 meq/gram.
- [28] Starches useful in preparing such grafted starch polymers include for example, indian corn starch, rice starch, waxy maize starch, waxy sorghum starch, tapioca starch, wheat starch, potato starch, pearl starch and sweet potato starch, and derivatives thereof. The derivatives include oxidized starches, hydroxyalkylated starches, carboxyalkylated starches, various solubilized starches, enzyme modified

starches, and the like. Generally, any starch can be used from which the vinyl monomer can be polymerized thereupon.

- [29] A polymer of this type is available from G-P Resins, Inc. under the Ambond® designation. One advantage of using such a material in the preparation of the sizing composition of the present invention is that a single component can provide the composition with both the required cationic agent as well as the film-forming binder component, described below in more detail.
- [30] The anionic and cationic polymers used to prepare the sizing composition of the present invention are generally aqueous solutions or aqueous dispersions of water-insoluble polymers. In the case of aqueous dispersions, the dispersed polymer particles or droplets of the anionic and cationic polymers generally are obtained by polymerizing the corresponding monomers in the presence of water. The polymerization is generally carried out according to well-known techniques. The resulting product typically is an aqueous dispersion (e.g., a latex) comprised of finely divided dispersed water-insoluble anionic or cationic polymer particles in aqueous solution, often containing a stabilizing agent.
- [31] Another important component of the sizing composition of the present invention is a film-forming binder, such as a polysaccharide. Any film-forming binder that is compatible with the blend of anionic and cationic polymers can be used. Exemplary film-forming binders include, but are not necessarily limited to: polysaccharides and derivatives thereof, e.g., starches, cellulosic polymers, dextran and the like; polypeptides (e.g., collagen and gelatin); and synthetic polymers, particularly synthetic vinyl polymers such as poly(vinyl alcohol), poly(vinyl phosphate), poly(vinyl pyrrolidone), vinyl-pyrrolidone-vinyl acetate copolymers, vinyl acetate-acrylic acid copolymers, vinyl alcohol-vinyl acetate copolymers, vinyl pyrrolidone-styrene copolymers, and poly(vinylamine), synthetic acrylate polymers and copolymers such as poly(acrylic acid-co-methacrylate), poly(vinyl-co-acrylate), and the like.
- [32] Generally, based on cost considerations the film-forming binder will be a polysaccharide such as a water-soluble alginate (sodium or potassium),

carboxymethyl cellulose, hydroxyethyl cellulose, or a starch. The polysaccharide is preferably a starch. Suitable starches may be any of a variety of natural, converted, and synthetically modified starches. Suitable starches include: barley, wheat, potato, corn, waxy maize, rice, tapioca, sorghum, and wheat. The starch may be converted or modified, e.g. treated with enzyme, acid, thermochemical treatment or oxidized. The starch may also be pregelatinized. The starch may also be chemically treated, e.g. by etherification, esterification, crosslinking, etc., to make it cationic, anionic or amphoteric. Starches that have been treated by a combination of the aforementioned processes also can be used, as can mixtures of the aforementioned starches. A preferred starch is a slightly anionic or slightly cationic starch.

- [33] As noted above, a particularly preferred source of the film-forming binder is a grafted starch, especially starches having a graft of a cationic polymer.
- [34] The various components of the sizing composition are added to form the size press solution or dispersion in a sequence to prevent any reciprocal interaction in the starch dispersion. For example, in order to make a size-press composition using a slightly cationic starch according the present invention, the anionic polymer additive is first added to the slightly cationic starch solution followed by the cationic polymer additive. If the starch is slightly anionic, then the cationic polymer additive is added prior to adding the anionic polymer additive. A suitable sequencing of the addition of the various constituents of the sizing composition to prevent any reciprocal interaction can be determined by a skilled worker using only routine experimentation. Generally, the various components can be combined a short time before using the composition to size paper.
- [35] The anionic and cationic polymers are present in the sizing composition in an amount sufficient to provide an essentially balanced charge. Generally, an essentially balanced charge can be obtained by providing the anionic and cationic polymers in a weight ratio of anionic polymer to cationic polymer of between about 0.2:1 to about 2.5:1, more usually the weight ratio is in the range of 0.4:1 to 2:1.

- [36] The film-forming polymer is generally present in the sizing composition in an amount of about 1 to about 18 percent by weight of the sizing composition, preferably in an amount of about 2 to about 12 percent by weight. Thus, a typical sizing composition for use as a size press solution will generally contain about 1 to about 18% by weight starch, often about 2 to about 12% by weight starch, in water with a pH between about 6 and 9.
- [37] The sizing composition will generally be provided in an aqueous liquid vehicle, as an aqueous solution or dispersion, although small amounts of a water-soluble or water miscible organic solvent may also be present. It may on occasion be necessary to add a solubilizing compound during preparation of the sizing composition so that the components dissolve in the aqueous liquid vehicle, e.g., an inorganic base such as ammonia and/or an organic amine. Suitable organic amines include lower alkyl-substituted amines such as methylamine, dimethylamine, ethylamine, and trimethylamine, as well as ethanolamine, diethanolamine, triethanolamine, and substituted ethanolamines, typically lower alkyl-substituted ethanolamines such as N-methyl and N,N-dimethyl ethanolamines, and morpholine. Such compounds are also useful for bringing the pH into the desired range for basic formulations, and, if present, will generally represent not more than about 1.0 wt. % of the composition, and in most cases will represent not more than about 0.5 wt. % of the composition.
- [38] The solids content of the aqueous solution or dispersion is influenced by the method selected for applying the size composition to the cellulosic substrate. In the case of conventional size presses, the size composition will typically have a solids content of about 1 to about 20 weight percent, *i.e.*, an amount of water between about 80 and about 99 weight percent. Suitable solids concentrations for the size compositions in other applications can be selected based on routine testing.
- [39] Thus, the amount of the anionic and cationic polymers added to the mixture to form the size press composition is preferably from about 0.05 to about 50 wt. %, more usually 0.05 to 25 wt. %, based on the total solids of the size press composition. More preferably the polymer solids level will be from about 0.1 to

about 20 wt. % based on the total solids. Usually, the polymer solids level will be from about 0.1 to about 15 wt. % based on the total solids and most often between about 0.5 and about 10 wt. %.

- [40] The specific techniques used to size paper and other cellulosic products such as cardboard, by means of the present invention are similar to those that are commonly employed in papermaking to apply the sizing composition to the cellulose-based product. For instance, the aqueous sizing composition may be applied to the surface of the paper using a size press by a calender or a doctor knife blade. Alternatively, the size composition may be sprayed onto the paper web or be applied by dipping the paper into the aqueous composition. The sizing composition also may be applied as part of the paper conversion process using conventional coating techniques. Paper treated with the sizing solution is then dried at elevated temperatures. Drying the paper web is sufficient to bring the surface size and surface strength to full development.
- [41] Thus, surface size treatment can be applied to paper as either a post-production operation or as a portion of the papermaking process itself. Surface size is applied typically in the papermaking process after the paper sheet has been formed and dried but not passed through a calendar stack. The formed and dried sheet (web) is conducted through a size press (actually a nip-coater of various configurations), which re-wets the sheet to some degree (depending on the type of size press) with the sizing composition. Upon the wetting or coating of the web, it is again dried and subsequently passed through a series of nips at the calendar to control caliper and smooth the finished sheet prior to wind-up and slitting or sheeting.
- [42] The size press composition is applied at the size press in an amount such that the level of starch and polymer solids applied to the surface is preferably about 0.02 wt. % to about 4.5 wt. % on a dry basis based on the weight of the dry sheet of paper. Usually, the level is about 0.025 wt. % to about 4.0 wt. %, and most often from about 0.05 wt. % to about 3.5 wt. %.
- [43] The sizing composition of this invention also may be used in conjunction with or serially with other additives conventionally used in the production of cellulose-

based products. Such additional additives may include, but are not necessarily limited to, inorganic fillers, anti-curl agents, or additional conventional components such as a surfactant, plasticizer, humectant, defoamer, UV absorber, light fastness enhancer, polymeric dispersant, dye mordant, optical brightener, or leveling agent, as are commonly known in the art.

- [44] The paper onto which the sizing composition is applied may vary widely and is independent of the kind of pulp used to make the paper. The paper may be a paper base produced by sheeting under the wide pH ranges of 4 to 9. Thus, the invention is suitable for the preparation of sized paper of any thickness and of any kind and thus applies to papers or cardboards obtained from mechanical, chemical, soda, sulphite, sulphate, semichemical, wood, natural vegetable, rag or old paper pulp and mixtures thereof.
- [45] The paper also may contain additives such as fillers, dyestuffs, paper strengthening agents, drainage rate improvers, and internal sizing agents. The surface sizing of previously internally sized paper is specifically contemplated. In particular, by using the invention in connection with a sheet that has been internally sized, that is, certain sizing agents have been added to the pulp suspension before it is converted to a paper sheet, one may obtain higher levels of surface sizing. Internal sizing tends to prevent or retard the surface size from soaking into the sheet, thus allowing it to remain on the surface where it has maximum effectiveness and may permit a lower surface size application rate at equivalent surface properties.
- [46] Internal sizing agents may include any of those commonly used at the wet end of a fine paper machine. These include rosin sizes, ketene dimers and multimers, alkenylsuccinic anhydrides and the like. The internal sizes are generally used at levels of from about 0.05 wt. % to about 0.25 wt. % based on the weight of the dry paper sheet.
- [47] When paper is sized in accordance with the present invention (a mixture of a film-forming binder and anionic polymer and cationic polymer additives), the paper has a degree of sizing that is equivalent to that when a starch-based sizing agent

that contains either an anionic or a cationic polymer is used. The sizing is typically manifested by an observation of improved surface hydrophobic properties (*i.e.*, higher HST test results).

- [48] When paper is processed in accordance with the present invention, the paper has a degree of surface strength that is greater than when a starch-based sizing agent that does not contain the blend of the anionic and cationic polymers is used. Improved surface strength is typically manifested by an observation of improved surface integrity (*i.e.*, lower Adam's Wet Rub test results).
- [49] In many cases one or more improved properties may be obtained simultaneously in a given product, but even if one only obtains a sized product having improved properties in one area and equivalent or even decreased properties in another area that result is often satisfactory. Those skilled in the art recognize the necessity or desirability of balancing the benefits of various improvements against costs, depending on particular circumstances.
- [50] It will be understood that while the invention has been described in conjunction with specific embodiments thereof, the foregoing description and following examples are intended to illustrate, but not limit the scope of the invention. Other aspects, advantages and modifications will be apparent to those skilled in the art to which the invention pertains, and these aspects and modifications are within the scope of the invention. Thus, the following examples are to be considered as exemplifying the invention, rather than limiting it in any way.
- [51] Throughout the specification and in the examples, "parts" means parts by weight.
- [52] Throughout the specification and in the examples, molecular weights are weight average, as measured by conventional, high pressure, size exclusion chromatography techniques using suitable molecular weight standards *e.g.* Pullulan polysaccharide standards.
- [53] The Hercules Sizing Test (HST) measures the rate of penetration of a 1 percent formic acid dye solution, read at 80% reflectance, as the solution penetrates through the sized paper. Skilled practitioners recognize that the HST test, results

reported as seconds, is a well-established test protocol for gauging the performance of a sized product. The test provides a relative evaluation of the hydrophobicity of a sized substrate.

- [54] The Adams Wet Rub test provides a measure of the amount of coating loss in a set time from a sample, as indicated by the turbidity of a water suspension. In the Adams Wet Rub Test, a moistened rubber roll, which passes through a moisturizing bath of fixed volume (formic acid solution of 1%), is rubbed against the sample (mounted on a backing roll) for a specified time and at a known pressure. The bath solution is collected and amount of coating removed from the sample is determined by measuring the turbidity of a given volume of water containing the abraded coating. Lower values indicate a higher level of surface integrity or strength.

Example 1

- [55] A base size press-solution includes 5.4% of a slightly anionic starch (Penford 280). In one case, an anionic polymer additive (NovaCote 1934) was added to the base solution. In another case, to the base starch solution was first added under stirring a cationic polymer additive (Amres 25 HP) and after 2 minutes the anionic polymer additive (NovaCote 1934) was added. The base paper used for sizing with each of the three compositions was a communication grade paper (15% ash) having a porosity (Gurley) of 16 seconds and an internal size (estimated by HST) of 2 seconds. The total pick up for each of the sizing compositions was 70 lb/ton. Based on this total pick-up, the calculated pick-ups for each of the sizing compositions are shown in Table 1. The drying temperatures were 103°C. Results of HST and Adams Wet Rub testing for each of the three samples are summarized in Table 1 below.

TABLE 1

SAMPLE	HST (sec.)	Adams Wet Rub (Turbidity units)
Starch only (70 lbs/ton)	10	32
NovaCote® 1934 (2 lb/ton)+ starch (68 lbs/ton)	28	45
NovaCote® 1934 (2 lb/ton) with AMRES (1 lb/ton)+ starch (67 lbs/ton)	36	4.6

Example 2

- [56] Size-press compositions were obtained by repeating the procedures of Example 1 except that NovaCote PS2 anionic polymer was substituted for NovaCote 1934 and Ambond 1520 was substituted for Amres. Again, the total pick up for each of the sizing compositions was 70 lb/ton. Based on this total pick-up, the calculated pick-ups for each of the sizing compositions are shown in Table 2. Results of HST and Adams Wet Rub testing are summarized in Table 2 below.

Table 2

SAMPLE	HST (sec.)	Adams Wet Rub (Turbidity units)
Starch only (70 lbs/ton)	10	32
Starch (68 lbs/ton) + NovaCote PS2 (2.0 lb/T)	50	13
Starch (68 lbs/ton) + Ambond 1520 (2.0 lb/T)	11	35
Starch (66 lbs/ton) + NovaCote PS2 (2.0 lb/T) + Ambond 1520 (2.0 lb/T)	74	10

Example 3.

- [57] A base size press composition was prepared which contained 3.5% of a slightly anionic starch (Penford 280). In one case, a size press composition was prepared by additionally adding an anionic polymer additive (NovaCote 1934). In another case, to this base starch solution was first added under stirring a cationic polymer additive (Amres 25 HP) and after 2 minutes an anionic polymer additive

(NovaCote 1934) was added. The base paper used with each of the three sizing compositions was a newsprint grade paper having a porosity (Gurley) of 40 seconds and an internal size (estimated by water drop method) of less than 1 second. The total solids pick-up from each of the sizing compositions was 55 lb/ton. Based on this total pick-up, the calculated pick-ups for each of the sizing compositions are shown in Table 3. The drying temperatures were 103°C. Results of sizing (water drop method) and of Adams Wet Rub testing for each of the sizing compositions are summarized in Table 3 below.

Table 3

SAMPLE	Water drop (sec.)	Adams Wet Rub (Turbidity units)
Starch only (55 lbs/Ton)	< 1.0	16
NovaCote® 1934 (1.7 lbs/Ton) plus starch (53.3 lbs/Ton)	16	7.0
NovaCote® 1934 (1.7 lbs/Ton) with AMRES (1lb/Ton) plus starch (52.3 lbs/Ton)	16	1.6

Example 4

- [58] A size-press composition was obtained by repeating the procedures of Example 3 except that NovaCote PS2 was substituted for NovaCote 1934. Test results are summarized in Table 4 below.

Table 4

SAMPLE	Water drop (sec.)	Adams Wet Rub (Turbidity units)
Starch only (55 lbs/Ton)	< 1.0	16
NovaCote® PS2 (1.7 lbs/ton) + starch (53.3 lbs/Ton)	259	3.5
NovaCote® PS2 (1.7 lbs/ton) with AMRES (1 lb/ton) + starch (52.3 lbs/Ton)	237	1.2

[59] The present invention has been described with reference to specific embodiments. However, this application is intended to cover those changes and substitutions that may be made by those skilled in the art without departing from the spirit and the scope of the invention. Unless otherwise specifically indicated, all percentages are by weight. Throughout the specification and in the claims the term "about" is intended to encompass $\pm$ or -5% .

I/We Claim:

1. A composition for improving surface size and surface strength for cellulosic products comprising an aqueous sizing mixture of a film-forming binder, an anionic polymer and a cationic polymer.
2. The composition of claim 1, wherein the film-forming binder is a starch.
3. The composition of claim 2 wherein the cationic polymer and starch are provided using a cationic polymer-grafted onto said starch.
4. The composition of claim 2 wherein the anionic polymer and starch are provided using an anionic polymer-grafted onto said starch.
5. The composition of claim 2 wherein the anionic polymer is an alkali soluble, acid-containing copolymer.
6. The composition of claim 5 wherein the anionic polymer is selected from the group consisting of a hydrolyzed copolymer of styrene-maleic anhydride, or one of its salts; a copolymer of styrene-maleic acid, or one of its salts; a styrene-acrylic acid copolymer, or one of its salts, a styrene-methacrylic acid copolymer, or one of its salts, a styrene-fumaric acid copolymer, or one of its salts, a styrene-acrylonitrile-acrylic acid copolymer, or one of its salts, a styrene-butyl acrylate-acrylic acid copolymer, or one of its salts; a copolymer of styrene-acrylic ester dispersed in a copolymer of styrene-maleic acid, or one of its salts, and mixtures thereof.
7. The composition of claim 5 wherein the cationic polymer is selected from the group consisting of a polyamine; a polyethylene imine; a styrene-maleic anhydride copolymer imide quaternary ammonium salt; a polyamidoamine-epichlorohydrin resin; a dialkylamine-epichlorohydrin resin; a homo- or copolymer of diallyldimethyl-ammonium chloride; a homo- or copolymer of a vinyl amine; a homo- or copolymer of a (meth)acrylamide; a homo- or copolymer of a (meth)acrylate, and corresponding acid addition salts and quaternary ammonium salts thereof.

8. The composition of claim 1 comprising a mixture of starch grafted with a copolymer of diallyldimethylammonium chloride-acrylamide and an alkali soluble, acid containing copolymer.

9. The composition of claim 2 comprising an anionic polymer latex having sulfonic or carboxylic moieties and a polyamidoamine-epichlorohydrin resin.

10. The composition of claim 2 comprising a copolymer of styrene-acrylic ester dispersed in a copolymer of styrene-maleic acid, or one of its salts and a polyamidoamine-epichlorohydrin resin.

11. The composition of claim 8 wherein the alkali soluble, acid containing copolymer is selected from the group consisting of a hydrolyzed copolymer of styrene-maleic anhydride, or one of its salts; a copolymer of styrene-maleic acid, or one of its salts; a styrene-acrylic acid copolymer, or one of its salts, a styrene-methacrylic acid copolymer, or one of its salts, a styrene-acrylonitrile-acrylic acid copolymer, or one of its salts, a styrene-butyl acrylate-acrylic acid copolymer, or one of its salts and mixtures thereof.

12. A composition for improving surface size and surface strength for cellulosic products comprising an aqueous sizing mixture of a film-forming binder, an anionic polymer and a cationic polymer, wherein the film-forming binder is a starch, wherein the anionic polymer is selected from the group consisting of a hydrolyzed copolymer of styrene-maleic anhydride, or one of its salts; a copolymer of styrene-maleic acid, or one of its salts; a styrene-acrylic acid copolymer, or one of its salts, a styrene-methacrylic acid copolymer, or one of its salts, a styrene-fumaric acid copolymer, or one of its salts, a styrene-acrylonitrile-acrylic acid copolymer, or one of its salts, a styrene-butyl acrylate-acrylic acid copolymer, or one of its salts; a copolymer of styrene-acrylic ester dispersed in a copolymer of styrene-maleic acid, or one of its salts, and mixtures thereof, wherein the cationic polymer is selected from the group consisting of a polyamine; a polyethylene imine; a styrene-maleic anhydride copolymer imide quaternary ammonium salt; a polyamidoamine-epichlorohydrin resin; a dialkylamine-epichlorohydrin resin; a homo- or

copolymer of diallyldimethyl-ammonium chloride; a homo- or copolymer of a vinyl amine; a homo- or copolymer of a (meth)acrylamide; a homo- or copolymer of a (meth)acrylate, and corresponding acid addition salts and quaternary ammonium salts thereof, and wherein the anionic and cationic polymers are provided in a weight ratio of anionic polymer to cationic polymer of between about 0.2:1 to about 2.5:1.

13. A method of sizing a cellulosic web comprising applying to a surface of the cellulosic web an aqueous sizing composition comprising a mixture of a film-forming binder, an anionic polymer and a cationic polymer.

14. The method of claim 13 wherein the film-forming binder is a starch.

15. The method of claim 14 wherein the cationic polymer and starch are provided using a cationic polymer-grafted onto said starch.

16. The method of claim 14 wherein the anionic polymer and starch are provided using an anionic polymer-grafted onto said starch.

17. The method of claim 14 wherein the anionic polymer is selected from the group consisting of a hydrolyzed copolymer of styrene-maleic anhydride, or one of its salts; a copolymer of styrene-maleic acid, or one of its salts; a styrene-acrylic acid copolymer, or one of its salts, a styrene-methacrylic acid copolymer, or one of its salts, a styrene-fumaric acid copolymer, or one of its salts, a styrene-acrylonitrile-acrylic acid copolymer, or one of its salts, a styrene-butyl acrylate-acrylic acid copolymer, or one of its salts; a copolymer of styrene-acrylic ester dispersed in a copolymer of styrene-maleic acid, or one of its salts, and mixtures thereof.

18. The method of claim 14 wherein the anionic polymer is an alkali soluble, acid containing copolymer

19. The method of claim 18 wherein the cationic polymer is selected from the group consisting of a polyamine; a polyethylene imine; a styrene-maleic anhydride copolymer imide quaternary ammonium salt; a polyamidoamine-epichlorohydrin resin; a

dialkylamine-epichlorohydrin resin; a homo- or copolymer of diallyldimethyl-ammonium chloride; a homo- or copolymer of a vinyl amine; a homo- or copolymer of a (meth)acrylamide; a homo- or copolymer of a (meth)acrylate, and corresponding acid addition salts and quaternary ammonium salts thereof.

20. The method of sizing of claim 13 wherein the aqueous sizing composition comprises a mixture of starch grafted with a copolymer of diallyldimethylammonium chloride-acrylamide and an alkali soluble, acid containing copolymer.

21. The method of claim 13 wherein the aqueous sizing composition comprises an anionic polymer latex having sulfonic or carboxylic moieties and a polyamidoamine-epichlorohydrin resin.

22. The method of claim 13 wherein the aqueous sizing composition comprises a copolymer of styrene-acrylic ester dispersed in a copolymer of styrene-maleic acid, or one of its salts and a polyamidoamine-epichlorohydrin resin.

23. The method of claim 20 wherein the alkali soluble, acid containing copolymer is selected from the group consisting of a hydrolyzed copolymer of styrene-maleic anhydride, or one of its salts; a copolymer of styrene-maleic acid, or one of its salts; a styrene-acrylic acid copolymer, or one of its salts, a styrene-methacrylic acid copolymer, or one of its salts, a styrene-acrylonitrile-acrylic acid copolymer, or one of its salts, a styrene-butyl acrylate-acrylic acid copolymer, or one of its salts and mixtures thereof.

24. A sized cellulosic web made by the method of claim 13, 14, 15, 16, 17, 18, 19, 20, 21, 22 or 23.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US2004/024195

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 D21H21/16

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)
 IPC 7 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, WPI Data

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☒ Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

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