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Description

TECHNICAL FIELD

[0001] This invention relates to a papermaking method in a papermaking process and, more specifically, to a papermaking method for improving retention and/or drainage property by adding an ionic water-soluble polymer prepared by a specific production method and an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite to pulp in a papermaking step.

BACKGROUND ART

[0002] Heretofore, the papermaking step has involved such a problem that a composition distribution in the direction of the thickness of a paper layer becomes nonuniform due to the effluence of various added fillers. There have also been such problems to be solved that cost is increased by the effluence of paper stuff and added chemicals and that the concentration of the paper stuff needs to be more than a predetermined value. The effluence of the fillers and the like causes the contamination of circulating white water. To solve these problems, a certain kind of retention aid is added.

[0003] Furthermore, an increase in the papermaking speed during papermaking leads to improvement of productivity whereas the increasing of the beating degree of pulp, which is desired from a view point of increasing paper strength, is contradictory to the papermaking speed. Therefore, it has been difficult to solve these at the same time. To solve the problem, a drainage aid is added.

[0004] As the retention aid or drainage aid is generally used a water-soluble polymeric substance, namely, a synthetic polymeric substance such as polyacrylamide or a derivative thereof, polyethylene-imine or polyamide polyamine epichlorohydrin resin, or a natural water-soluble polymeric substance such as starch or a derivative thereof.

[0005] For the purpose of further improving retention and/or drainage property, various methods have been proposed. They include one in which colloid silica is added to paper stuff for making paper after cationic or amphoteric water-soluble polymer is added as described in JP-A-3-027676, one in which cationic starch or Hoffmann reaction product of polyacrylamide is added to paper stuff after anionic acrylamide-based polymer having anionic groups of 25-60 mol% and having a molecular weight of one hundred thousand to one million (JP-A-60-195900), one in which cationic starch and anionic colloidal silica are used (JP-A-57-051900, corresponding to EP-A-0 041 056), one in which an acrylamide-based polymer having cationic groups and colloidal silica are used (JP-A-62-015391), one in which colloidal silicic acid, cationic or amphoteric polyacrylamide derivative and cationic starch are added (JP-A-62-110998), one in which a cationic polymer and bentonite are used to improve retention (JP-A-62-191593, corresponding to EP-A-0 235 393). In addition, there are known methods, one in which firstly a cationic polymer having a high molecular weight is added to cellulose slurry of paper stuff and secondly an anionic polymer having a middle molecular weight is added (JP-A-4-245998, corresponding to US-A-5 098 520), one in which a mixture of an anionic polymeric substance and bentonite is added to paper stuff after a cationic polymer polymeric substance and bentonite is added to paper stuff after a cationic polymer flocculant is added (JP-A-64-61588) and the like.

[0006] Although these methods improve retention or drainage property more than a method in which a water-soluble polymer is used alone, they are not satisfactory because of the worsening situation of paper stuff, deterioration in the quality of water for papermaking and the like caused by recent progress in the papermaking technology and increased use of recycled pulp. Therefore, a method for further improving retention or drainage property is strongly desired.

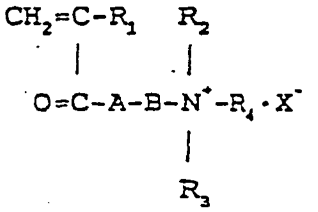
[0007] It is therefore an object of the present invention to improve productivity in papermaking and drying steps by improving the yields of cellulose fibers, fillers and the like and/or drainage property in the papermaking process. More specifically, it is an object of the present invention to produce high-quality paper by making uniform a composition distribution in the direction of the thickness of a paper layer, to reduce cost by preventing the effluence of paper stuff and fillers, and not to reduce the papermaking speed even when paper is produced from pulp having a high beating degree. Another object of the present invention is to establish a stable papermaking method by keeping circulating white water clean by improving retention and/or drainage property. A further object of the present invention is to provide a papermaking method which is intended to reduce a load in a white water recovery step and a load in a waste water treatment step by improving retention and/or drainage property

DISCLOSURE OF THE INVENTION

[0008] The inventors of the present invention have conducted intensive studies to attain the above objects and have found that the above objects can be attained by a papermaking method for improving retention and/or drainage property by adding an ionic water-soluble polymer obtained by the following dispersion polymerization method to paper stuff and mixing them, and then adding and mixing an anionic additive selected from the group consisting of organic anionic (co) polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite in the papermaking step.

The present invention as described in claim 1 is based on this finding.

[0009] The dispersion polymerization method for the ionic water-soluble polymer used in the present invention is a polymerization method for obtaining a dispersion of fine polymer particles by polymerizing (A) 3 to 100 mol% of a water-soluble cationic vinyl monomer represented by the following formula (1) or a mixture thereof, (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer and (C) the remainder consisting of a water-soluble nonionic vinyl monomer, based on the total of all the monomers, under agitation in an aqueous salt solution capable of dissolving the monomers but not the produced polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous salt solution.



$$CH_2=C(R_1)-C(=O)-A-B-N^{+}(R_2)(R_3)-R_4\cdot X^{-} \qquad (1)$$

(wherein A is O or NH; B is C_2H_4, C_3H_6 or C_3H_5OH; R_1 is H or CH_3; R_2 and R_3 are each CH_3 or C_2H_5; R_4 is H, CH_3, C_2H_5 or benzyl group; and X^- is an anionic counter ion.)

[0010] In other words, the present invention is a papermaking method comprising the steps of adding to paper stuff in a papermaking step an ionic water-soluble polymer produced by a polymerization method called dispersion polymerization for obtaining a dispersion of fine polymer particles by polymerizing specific water-soluble ionic vinyl monomers under agitation in an aqueous salt solution capable of dissolving the monomers but not the produced polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous salt solution, and then adding an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite so as to improve retention and/or drainage property.

[0011] The present invention further provides a papermaking method in which a salt forming the aqueous salt solution used in the production of the ionic polymer used in the above method is a divalent anionic salt.

[0012] The present invention further provides a papermaking method in which the dispersant used in the production of the ionic polymer used in the above method is a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of at least one cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 0 to 50 mol% of acrylamide.

[0013] The present invention further provides a papermaking method in which the intrinsic viscosity of the ionic water-solution polymer in a 2 wt% ammonium sulfate aqueous solution is 5 dl/g to 30 dl/g in the above method.

[0014] The present invention further provides a papermaking method in which the ionic water-soluble polymer is added in an amount of 0.001 to 0.2 wt% of the suspended substance of the paper stuff (called as "paper stuff SS") and the anionic additive is added in a total amount of 0.001 to 0.5 wt% of the paper stuff SS. In this instance, the ionic polymer is preferably added in an amount of 0.001 to 0.05 wt% and the anionic additive is preferably added in a total amount of 0.01 to 0.2 wt%.

[0015] The present invention still further provides a papermaking method in which the anionic additive, which is added after the ionic polymer is added and mixed, is anionic (co)polymer comprising acrylic acid of 15~100 mol% and acrylamide of 0~35 mol% based on the total of all the monomers.

[0016] The present invention still further provides a papermaking method in which the anionic additive, which is added after the ionic polymer is added and mixed, is anionic (co)polymer polymerized in a aqueous salt solution capable of dissolving the monomers but not the produced polymer, and a water-diluted dispersion of the resulted polymer fine particles is added thereto as said anionic additive.

[0017] The present invention further provides a papermaking method in which the ionic water-soluble polymer is added prior to the centrifugal screening of the papermaking process and the anionic additive is added after the centrifugal screening in the above method.

[0018] The present invention is a papermaking method in which the ionic water-soluble polymer contains a water-soluble anionic vinyl monomer in an amount of 1 to 30 mol% of the total of all the monomers in the above method. In this instance, the anionic monomer is preferably at least one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, acrylamide-2-methylpropanesulfonic acid and salts thereof, and mixtures thereof, the most preferably acrylic acid.

[0019] The present invention is a papermaking method in which the gram equivalent of the water-soluble cationic vinyl monomer used in the ionic water-soluble polymer is greater than the gram equivalent of the water-soluble anionic vinyl monomer in the above method.

[0020] The present invention provides a papermaking method in which the ionic water-soluble polymer does not contain a water-soluble anionic vinyl monomer in the above method.

[0021] The present invention further provides a papermaking method in which the water-soluble nonionic vinyl monomer is acrylamide in the above method.

[0022] The present invention further provides a papermaking method in which the water-soluble cationic vinyl monomer is a tertiary salt and/or quaternary product of dimethylaminoethylacrylate in the above method.

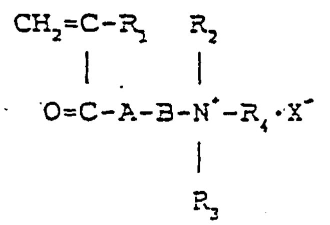
BEST MODE FOR CARRYING OUT THE INVENTION

[0023] A method for producing an ionic water-soluble polymer used in the present invention is dispersion polymerization for obtaining a dispersion of the ionic water-soluble polymer by polymerizing water-soluble ionic vinyl monomers under agitation in an aqueous salt solution capable of dissolving the monomers used but not the produced ionic water-soluble polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous solution. This method is disclosed in EP-A-0183466 and EP-A-0364175.

[0024] The inventors of the present invention have found that, when the ionic water-soluble polymer produced by dispersion polymerization in an aqueous salt solution is used in combination with an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite it greatly improves retention and/or drainage property, compared with an ionic water-soluble polymer having the same monomer composition and produced by a conventional polymerization method such as polymerization in an aqueous solution or water-in-oil type emulsion polymerization. The present invention is predicated upon this finding.

[0025] This is considered to be caused by the characteristic feature of the dispersion polymerization in an aqueous salt solution. In this polymerization method, the monomers are uniformly dissolved in the aqueous salt solution, which is a polymerization solvent, before polymerization. However, as the polymerization proceeds, the produced polymer separates out from the aqueous salt solution and forms a dispersion of fine particles with the aid of a dispersant. That is, phase separation from a uniform phase to double phases takes place. Although this polymerization mechanism has not been elucidated yet, it is assumed that a polymer having a specific molecular structure, such as a branched polymer or block copolymer, is produced unlike polymerization in an aqueous solution or water-in-oil type emulsion polymerization in which polymerization is carried out in a uniform phase. It can be considered that this specific molecular structure is a primary factor of improving retention and/or drainage property.

[0026] The water-soluble cationic vinyl monomer constituting the ionic water-soluble polymer used in the present invention is represented by the following formula (1);



$$CH_2{=}C(R_1)-C({=}O)-A-B-N^{+}(R_2)(R_3)-R_4\cdot X^{-} \qquad (1)$$

(wherein A is O or NH; B is C_2H_4, C_3H_6 or C_3H_5OH; R_1 is H or CH_3; R_2 and R_3 are each CH_3 or C_2H_5; R_4 is H, CH_3, C_2H_5 or benzyl group; and X^- is an anionic counter ion.).

[0027] Preferred examples of the water-soluble cationic vinyl monomer represented by the above formula (1) include tertiary salts and/or quaternary products of dimethylaminoethylacrylate and dimethylaminoethylmethacrylate, and tertiary salts and/or quaternary products of dimethylaminopropylacrylamide and dimethylaminopropylmethacrylamide.

[0028] Typical examples of the tertiary salt include hydrochlorides and sulfates of the above monomers and typical examples of the quaternary product include methylated, ethylated and benzylated products of the above monomers.

[0029] Illustrative examples of the water-soluble cationic vinyl monomer represented by the above formula.(1) include acryloyloxyethyldimethylbenzylammonium chloride, methacryloyloxyethyldimethylbenzylammonium chloride, acrylamidepropyldimethylbenzylammonium chloride, methacrylamidepropyldimethylbenzylammonium chloride, acryloyloxyelhyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, hydrochloride salt or sulfuric acid salt oi dimethylaminoethylacrylate, hydrochloride salt or sulfuric acid salt of dimethylaminoethylmethacrylate, hydrochloride of dimethylaminoethylacrylate, hydrochloride salt or sulfuric acid salt of dimethylaminoethylmethacrylate, hydrochloride salt or sulfuric acid salt of dimethylaminopropylacrylamide, hydrochloride salt or sulfuric acid salt of dimethylaminopropylmethacrylamide, and the like. Out of these, particularly preferred water-soluble cationic vinyl monomer as a monomer containing a benzyl group is acryloyloxyethyldimethylbenzylammonium chloride and preferred water-soluble cationic vinyl monomer as a monomer containing no benzyl group is acryloyloxyethyltrimethylammonium chloride.

[0030] Examples of the water-soluble anionic vinyl monomer used in the present invention include, for example, itaconic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, acrylic and methacrylic anionic monomers, and mixtures thereof.

[0031] Typical acrylic and methacrylic anionic monomers include acrylic acid, methacrylic acid and salts thereof, 2-acrylamide-2-methylpropanesulfonic acid and salts thereof, and mixtures thereof. Out of these, preferred water-soluble anionic vinyl monomers are acrylic acid and methacrylic acid, and the most preferred is acrylic acid.

[0032] Examples of the water-soluble nonionic vinyl monomer used in the ionic water-soluble polymer of the present invention include, for example, acrylamide, methacrylamide, hydroxyethylacrylaie, hydroxyethylmethacrylate and the like. From a view point of improving retention and/or drainage property as a chemical for papermaking, acrylamide is the most preferred.

[0033] The ionic water-soluble polymer used in the present invention is obtained by polymerizing (A) 3 to 100 mol% of a water-soluble cationic vinyl monomer represented by the above formula (1), (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer and (C) the remainder consisting of a water-soluble nonionic vinyl monomer based on the total of all the monomers.

[0034] The above ionic water-soluble polymer used in the present invention is preferably a cationic or amphoteric water-soluble polymer. As an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite is anionic, use of an anionic or nonionic water-soluble polymer is not preferred as a polymer to be first added.

[0035] When the above ionic water-soluble polymer is a cationic water-soluble polymer, out of the vinyl monomers represented by the above formula (1), a homopolymer of a water-soluble cationic vinyl monomer containing a benzyl group, or a copolymer of a plurality of vinyl monomers represented by the above formula (1) or a copolymer thereof further comprising a water-soluble nonionic vinyl monomer such as acrylamide or methacrylamide is preferred. Although a preferred molar ratio of these monomers is not particularly limited, such a molar ratio is essential that the aqueous salt solution serving as a polymerization solvent does not dissolve the produced ionic water-soluble polymer or salts out the produced ionic water-soluble polymer.

[0036] For example, a preferred range of the molar ratio is such that a polymer comprising 3 to 100 mol % of a water-soluble cationic vinyl monomer containing a benzyl group and represented by the above formula (1) or a mixture thereof, 0 to 50 mol% of another water-soluble cationic vinyl monomer containing no benzyl group and represented by the above formula (1) or a mixture thereof, and the remainder consisting of a nonionic monomer is salted out.

[0037] The monomer containing a benzyl group which is the water-soluble cationic vinyl monomer of the above formula (1) has an amino group bonded to the very hydrophobic benzyl group. As a result, the produced polymer hardly dissolves in the aqueous salt solution though it is a water-soluble polymer. Therefore, when the cationic water-soluble polymer contains a benzyl group-containing water-soluble cationic vinyl monomer of the above formula (1) as a constituent element, a molar ratio of the monomer to another water-soluble cationic vinyl monomer of the above formula (1) having no benzyl group can be set to a wide range.

[0038] Meanwhile, when the cationic water-soluble polymer contains a water-soluble cationic vinyl monomer represented by the above formula (1) and having no benzyl group as a constituent element, the molar ratio of the water-soluble cationic vinyl monomer to acrylamide or methacrylamide is preferably in the range of 3:97 to 30:70.

[0039] The amphoteric water-soluble polymer as the ionic water-soluble polymer used in the present invention is preferably a copolymer comprising 3 to 99 mol% of a water-soluble cationic vinyl monomer represented by the above formula (1) or a mixture thereof, 1 to 30 mol% of the above water-soluble anionic vinyl monomer, and the remainder consisting of a water-soluble nonionic vinyl monomer such as acrylamide or methacrylamide. Although a preferred molar ratio of these monomers is not particularly limited, such a molar ratio is essential that the aqueous salt solution serving as a polymerization solvent does not dissolve the produced polymer or salts out the produced polymer.

[0040] However, in order to make the amphoteric water-soluble polymer remarkably show its characteristic features, all the ionic vinyl monomers, both cationic and anionic, are preferably contained in the copolymer in an amount of 5 mol% or more, more preferably 10 mol% or more. When all the ionic vinyl monomers are contained in the copolymer in a amount of less than 5 mol%, retention, drainage and other properties will be unsatisfactory.

[0041] As for the molar ratio of each ionic vinyl monomer, the gram equivalent of the water-soluble cationic vinyl monomer is preferably greater than the gram equivalent of the water-soluble anionic vinyl monomer because it is preferred that the amphoteric copolymer contains more cationic groups than anionic groups. Particularly preferably, the gram equivalent value of the cationic groups is at least two times or more the gram equivalent value of the anionic groups.

[0042] A more preferred example of the above amphoteric water-soluble polymer is a dispersion copolymer comprising 3 to 99 mol% of a water-soluble cationic vinyl monomer containing a benzyl group, out of water-soluble cationic vinyl monomers represented by the above formula (1), or a mixture thereof, 0 to 50 mol% of another water-soluble cationic vinyl monomer represented by the above formula (1) or a mixture thereof, 1 to 30 mol% of the above water-soluble anionic vinyl monomer and the remainder consisting of acrylamide.

[0043] Another preferred example of the above amphoteric water-soluble polymer is a dispersion copolymer comprising 3 to 30 mol% of a water-soluble cationic vinyl monomer containing no benzyl group and represented by the above formula (1); to 30 mol% of an anionic monomer and the remainder consisting of acrylamide.

[0044] Further, monomers other than the above monomers, for example, hydrophobic monomers such as acrylonitrile, methylacrylate, ethylacrylate, 2-ethylhexylacrylate and styrene may be copolymerized if the produced copolymer is water-soluble.

[0045] Polymerization is carried out in the presence of a dispersant while a plurality of monomers are stirred in an aqueous salt solution. The total concentration of the monomers at this point is preferably 5 wt% or more, more preferably 10 wt% or more, the most preferably 15 to 40 wt%. When the total concentration of the monomers is less than 5 wt%, the concentration of the polymer in the aqueous dispersion becomes low and thus it is economically disadvantageous.

[0046] It is an essential requirement that the aqueous salt solution which serves as a polymerization solvent and dispersion medium used in the present invention at the time of producing a polymer should not dissolve the produced polymer or should salt out the produced polymer. That is, a combination of the composition of the monomers of the ionic water-soluble polymer and the type and concentration of the salt that satisfies this condition is essential.

[0047] The salt used in the aqueous salt solution is preferably a polyvalent anionic salt. Typical examples of the salt include sodium sulfate; ammonium sulfate, magnesium sulfate, aluminum sulfate, disodium hydrogen phosphate and the like. Other salts may be used if the aqueous salt solutions thereof dissolve the monomers and the dispersant and do not dissolve the produced polymer. Out of these, sulfates are preferred. In terms of valence, divalent anionic salts are preferred. More specifically, ammonium sulfate and sodium sulfate are the most preferred.

[0048] The concentration of the salt in a reaction solution during the polymerization process vary depending on the molar ratio of the water-soluble cationic vinyl monomer represented by the above formula (1), the molar ratio of the water-soluble anionic vinyl monomer and the type of the salt used, and hence, is not particularly limited.

[0049] However, the concentration of the salt in the reaction solution during the polymerization process is preferably between 15 wt% based on the polymerization solvent obtained by subtracting the weight of the monomers from the weight of the polymerization reaction solution and the saturation concentration, or between 15 wt% and the limit of solubility, more preferably between 15 wt% and 30 wt%; the most preferably between 15 wt% and 25 wt%. If the concentration of the salt is less than 15 wt%, the viscosity of the reaction solution under reaction becomes too high to make it difficult to successfully complete the polymerization process.

[0050] Although a salt is added to a solvent at the time of polymerization, part of the salt may alternatively be added to the dispersion after the completion of polymerization. The viscosity of the dispersion can be made lower when part of the salt is added to the dispersion after the completion of the polymerization process than that when the salt is all added to the solvent at the time of polymerization. The concentration of the salt in the dispersion obtained by adding part of it to the dispersion after the completion of the polymerization process is preferably between 15 wt% and the saturated concentration or between 15 wt% and the limit of solubility, more preferably between 15 wt% and 25 wt%.

[0051] Any combination of the composition of monomers in which a produced polymer is not salted out even by changing the type of the salt or the concentration of the salt or the composition of monomers of an ionic water-soluble polymer in which the salting-out of a produced polymer does not occur and the type and concentration of the salt is out of the scope of the present invention.

[0052] It is an essential requirement that the dispersant composed of a polymer electrolyte which is present at the time of polymerization is soluble in the aqueous salt solution.

[0053] A cationic polymer electrolyte is preferably used as the polymer electrolyte because a cationic polymer is preferred as an ionic polymer which is the product and the gram equivalent value of the cationic monomer contained in the amphoteric polymer is preferably greater than the gram equivalent value of the anionic monomer contained therein. The dispersant is more preferably a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of at least one cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 50 to 0 mol% of acrylamide.

[0054] The amount of the polymer electrolyte dispersant is about 1 to 15 wt%, preferably about 1 to 10 wt%, based on the total weight of all the monomers. If the amount is less than 1 wt%, the produced polymer cannot be obtained in a dispersed state and undesirably agglomerates to a large mass. If the amount, is more than 15. wt%; the viscosity of the finally obtained dispersion is undesirably too high to lose easy flowability.

[0055] In the present invention, the polymerization process can be initiated by any known method if the resulting polymer can be obtained in the form of a dispersion. However, it is preferable to use a.polymerization initiator therefor.

There are no limitations to the selection of a polymerization initiator, but generally a tree-radical initiator may be preferably used. The polymerization initiator may preferably be selected from those of a redox type, those of an azo type and those of any other types. Examples of the redox type initiator include combinations of one selected from ammonium peroxosulfate, potassium peroxodisulfate, hydrogen peroxide, and benzoyl peroxide, and one selected from sodium hydrogen sulfite, ferrous sulfate, tetramethylethylenediamine, and dimethylaniline. Examples of the azo type initiator include 2,2'-azobis(2-amidinopropane)dihydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile). Examples of the other type initiator include ammonium peroxosulfate, potassium peroxodisulfate, hydrogen peroxide, acetyl peroxide, lauroyl peroxide, benzoyl peroxide, cumene hydroperoxide; di-tert.-butyl peroxide, tetramethylthiuram disulfide, dibenzoyldisulfide, and p-toluenesulphinic acid.

[0056] In addition, for the purpose of the present invention, there are no specific limitations to the polymerization temperature so far as the polymerization initiator works properly at the selected temperature. As for the type of the polymerization initiator, 2, 2'-azobis(2-amidinopropane)dihydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride and the like are preferred because they are water-soluble, easily handled and controllable.

[0057] The polymer dispersion contains the ionic water-soluble polymer at a high concentration equal to or higher than 5 wt%, normally at a level between 5 wt% and about 40 wt%. The dispersion contains the above salt and above dispersant.

[0058] While the dispersion contains an ionic water-soluble polymer at a high concentration, its viscosity is normally as low as 10 to 3000 mPa·S because the ionic water-soluble polymer is stably dispersed in the aqueous salt solution in the form of fine particles. Thus, it is easily flowable and extremely easy to be handled.

[0059] The average particle diameter of the particles of the ionic water-soluble polymer in the above dispersion is normally 0.1 to 150 μm, preferably 0.1 to 50 μm, more preferably 0.1 to 30 μm. If the average particle diameter of the particles of the ionic water-soluble polymer exceeds 150 μm, they can easily precipitate to damage the stable storability of the dispersion and require a long time before they are completely dissolved into water because of low solubility due to the large sizes of the particles of the ionic water-soluble polymer if the dispersion is mixed with water for use.

[0060] There are no specific limitations to the molecular weight of the ionic water-soluble polymer in the above dispersion. However, it preferably has a large molecular weight when it is used in a papermaking process. When the dispersion of the ionic water-soluble polymer is dissolved in a 2 wt% aqueous solution of ammonium sulfate, the intrinsic viscosity of the polymer is normally found within a range of 5 dl/g to 30 dl/g. If the intrinsic viscosity is less than 5 dl/ g, the effect of improving retention and/or drainage property will be insufficient and if the intrinsic viscosity is more than 30 dl/g, the formation of paper will become worse, giving an ill effect on the quality of the produced paper.

[0061] The above dispersion is stably storable and is free from the problem of agglomerating to a large mass even if stored at room temperature.

[0062] In the present invention, the anionic additive is one selected from the group consisting of organic anionic (co) polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite.

[0063] The anionic colloidal silica used in the present invention is produced by maintaining an aqueous solution of sodium orthosilicate at a pH value of 1 to 4 and a commercial product can be used. The anionic colloidal silica is generally a silicon dioxide having an OH group on the surface by hydration in water and a porous particle surface generally charged with negative (-) electricity in water. More specifically, the anionic colloidal silica is a colloidal silicic acid sol having a surface area of about 50 to about 1,000 m^2/g, preferably about 300 to about 700 m^2/g or colloidal silica containing about 20 to 90 % of this colloidal silicic acid sol as disclosed in said JP-A-57-057 900. Long and narrow anionic silica sol having a particle diameter measured by a dynamic light scattering method of about 40 to 300 nm and an uniform thickness of about 5 to 20 nm, and showing extension on the same plane is preferably used.

[0064] As the bentonite, a commercial product can be used.

[0065] The anionic (co)polymer used in the present invention is a polymer or a copolymer comprising anionic monomers of which structure includes an anionic group. Examples of the anionic monomer are preferably one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, acrylamide-2-methylpropanesultonic acid and salts thereof, and a mixture thereof. The most preferred anionic monomer is acrylic acid, namely, the anionic (co)polymer is preferably an acrylic acid (co)polymer. In addition to the above monomers, other monomers can be copolymerized, i.e., nonionic monomer, e.g., methacrylamide, acrylonitrile, methacrylonitrile, methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, hydroxyethylacrylate, hydroxyethylmethacrylate, and the like.

[0066] It is preferred that the acrylic acid (co)polymer comprises acrylic acid of 15~100 mol% and acrylamide of 0~85 mol% based on the total of all the monomers.

[0067] In the present invention the preparative method of the used anionic (co)polymer should not be limited, and thus any known methods can be applied. Out of them, polymerizing methods for obtaining fine polymer particles by polymerizing in an aqueous salt solution capable of dissolving the monomers but not the produced polymer is preferred.

[0068] The prepared anionic (co)polymer preferably has a molecular weight of 1.5 million or more. The prepared polymer is added to paper stuff as a water-diluted dispersion of the resulted polymer fine particles.

[0069] In the papermaking step, the dosage of the ionic water-soluble polymer is preferably 0.001 to 0.2 wt% based on the weight of the paper stuff SS, and the total dosage of the anionic additive is preferably 0.001 to 0.5 wt% based on the weight of the paper stuff SS.

[0070] Further, the dosage of the ionic water-soluble polymer is more preferably 0.001 to 0.05 wt% based on the weight of the paper stuff SS and the total dosage of the anionic additive is more preferably 0.01 to 0.2 wt% based on the weight of the paper stuff SS.

[0071] When the dosage of the chemical(s) is too small, the effect is reduced and when the dosage is too large, waste materials on felt or wires used in the papermaking step is liable to occur.

[0072] In the papermaking method of the present invention, the time for adding each additive is not particularly limited. However, the ionic water-soluble polymer needs to be first added, followed by an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite. Preferably, in the papermaking step, the ionic water-soluble polymer is added before the centrifugal screening of the papermaking process and the anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite added after the centrifugal screening.

[0073] After the addition of the ionic water-soluble polymer, it is preferred that the polymer is uniformly distributed to the surface of a suspended substance by suitable shearing. After the addition of the anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite, it is desirable to prevent the destruction of an agglomerate caused by mixing excessively

[0074] According to the present invention, the ionic water-soluble polymer produced by dispersion polymerization in an aqueous salt solution greatly improves retention and/or drainage property when used in combination with an anionic additive selected from the group consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite, compared with an ionic water-soluble polymer having the same monomer composition and produced by a conventional polymerization method such as aqueous solution polymerization or water-in-oil type emulsion polymerization.

[0075] As described above, according to dispersion polymerization in an aqueous salt solution, as polymerization proceeds, the produced polymer separates out from the aqueous salt solution which serves as a polymerization solvent. Therefore, a specific molecular structured polymer such as branched polymer is produced unlike polymerization which is carried out in a uniform phase, and this specific molecular structure is assumed to be the primary factor of improving retention and/or drainage property.

EXAMPLES

[0076] The present invention will be described in greater detail by way of examples hereinafter, although the scope of the present invention is by no way limited by the following examples.

(Preparation Examples of Ionic Polymer)

(Nos. 1 to 6)

[0077] 4.2 g of polyacryloyloxyethyltrimethylammonium chloride as a dispersant and B4.0 g of ammonium sulfate as a separating agent were dissolved in 303.0 g of ion exchanged water in a 1-liter five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet. 100.0 g of each of monomers having respective compositions shown in Table 1 was charged into the flask, followed by heating them to 50°C and the air inside was displaced with nitrogen. 2.0 g of a 1 % aqueous solution of 2,2'-azobis(2-amidinopropane)dihydrochloride was further added thereto as a polymerization initiator and the polymerization operation was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in an aqueous salt solution. To this reaction mixture was added 21 g of ammonium sulfate to obtain dispersed polymer samples A to F to be used in the present invention.

[0078] The monomer compositions and intrinsic viscosities in a 2 wt% aqueous solution of ammonium sulfate of the dispersed polymer samples A to F are shown in Table 1.

(Nos. 7 to 12)

[0079] For comparison, monomers having respective compositions shown in Table 1 were used to obtain comparative samples a to f by aqueous solution polymerization and reverse-phase emulsion polymerization similarly.

[0080] The monomer compositions and intrinsic viscosities in the 2 wt% aqueous solution of ammonium sulfate of the comparative samples a to f are shown in Table 1.

Table 1

No.	Ionic Polymer Sample	Monomer Composition Ratio (mol%)				Intrinsic Viscosity (dl/g)	Polymerization Method
		ABC	DMQ	AAc	AAm		
1	A	15	0	. 0	85	5.8	(1)
2	B	0	10	0	90	6.2	(1)
3	C	15	0	5	80	13.6	(1)
4	D	10	10	10	70	14.6	(1)
5	E	40	20	0	40	7.8	(1)
6	F	40	20	20	20	12.4	(1)
7	a	15	0	0	85	7.2	(2)
8	b	0	10	0	90	6.3	(2)
9	c	15	0	5	80	14.0	(2)
10	d	10	10	10	70	14.6	(2)
11	e	40	20	0	40	7.8	(3)
12	f	40	20	20	20	13.8	(3)

*ABC: acryloyloxyethyldimethylbenzylammonium chloride
DMQ: acryloyloxyethyltrimethylammonium chloride
AAc: acrylic acid
AAm: acrylamide
(1): Dispersion polymerization
(2): Aqueous solution polymerization
(3): Reverse-phase emulsion polymerization

(Preparation of Acrylic (Co)Polymer)

[0081] 96 g of a 50 wt% aqueous solution of acrylamide, 12 g of acrylic acid and 46.5 g of sodium sulfate were dissolved in 145.5 g of ion exchanged water in a 500-milliliter five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet, followed by heating them to 25°C by means of a water bath and the air inside was displaced with nitrogen while stirring for 30 minutes. 0.6 ml of a 10 wt% aqueous solution of ammonium persulfate and 0.6 ml of a 10 wt% aqueous solution of sodium hydrosulfite were added thereto as a polymerization initiator and the polymerization operation was conducted with stirring. After 2 minutes, the solution was whitened. At this time, the water bath was removed and the temperature inside was about 70°C after 30 minutes by the heat of polymerization. After then, the polymerization temperature was maintained by a 70°C water bath for 2 hours and the polymerization reaction was completed.

[0082] The prepared acrylic acid-acrylamide copolymer had a viscosity of 320 mPa·S measured by a Brooke-field viscometer. According to the microscopic investigation, an average diameter of the prepared copolymer particles was 5 μm and thus the resulted polymer was obtained in a form of a dispersion. The prepared dispersion (20 wt% polymer concentration) was diluted by ion exchanged water into 1/40 concentration and the viscosity of the diluted dispersion was 3.0 mPa·S measured by a Brooke-field viscometer where the polymer was not dissolved. The polymer was neutralized by sodium hydroxide and the intrinsic viscosity in 1 N sodium chloride aqueous solution was 6.0 dl/g. The prepared acrylic acid-acrylamide copolymer dispersion is designated as sample G.

[0083] A dispersion of homopolymer of acrylic acid was prepared by the same preparative method as above. The dispersion is designated as sample H. The intrinsic viscosity of the sample H in 1N sodium chloride aqueous solution is 6.1 dl/g.

(Comparative Examples 1 to 14)

[0084] A retention test was conducted by adding the ionic polymer dispersions (A) to (F) to paper stuff.

[0085] 15 wt% (based on the weight of pulp) of ground calcium carbonate was added as a filler to bleached kraft pulp of broad-leaved tree (L-BKP) [Canadian standard freeness (C.S. F) = 330] to adjust the concentration of SS to 0.5 wt%.

[0086] Using this slurry, the retention rate was measured by a Britt-type dynamic jar tester.

[0087] The test was conducted in the following procedure.

[0088] 500 ml of 0.5 wt% paper stuff was put into the Britt-type dynamic jar tester.

[0089] Stirring was started at 1,500 rpm and a 0.1 wt% aqueous solution of each of the cationic polymers obtained in the above preparation examples was added. At this point, time counting was started.

[0090] After 30 seconds, 0.1 wt% bentonite (trade name: Organosob-O, manufactured by Allied Colloid Co.) and/or 0.1 wt% anionic colloidal silica (trade name: SMA-780, manufactured by Nissan Ekanobel Co.) were/was added.

[0091] After another 30 seconds, a white water sampling cock was opened to flow in white water which has passed through a wire of 150 mesh.

[0092] The white water was thrown away for the initial 10 seconds and then collected for the succeeding 30 seconds. The amount of the white water during this time is represented by X (ml).

[0093] The white water was filtered by a quantitization filter paper (No. 5C of Toyo Filter Co.) which has a dry weight of W_0 (g) at t05°C, dried at 105°C and measured for its weight. This weight is represented by W_1(g).

[0094] Thereafter, the white water with the quantitization filter paper was incinerated at 600°C and the weight of the ash content of the white water was measured. This weight is represented by f(g).

[0095] The SS concentration and the ash concentration of the white water are obtained from the following equations.

$$\text{SS concentration of white water (wt\%)} = \frac{W_1 - W_0}{X} \times 100 = SS_1$$

$$\text{ash concentration of white water (wt\%)} = \frac{f}{X} \times 100 = Ash_1$$

[0096] The SS concentration and the ash concentration were also measured for 0.5 wt% paper stuff. They are represented by SS_0 and Ash_0, respectively.

[0097] The total one pass retention and filler one pass retention were calculated from the following equations.

$$\text{total one pass retention (T-OPR\%)} = \frac{SS_0 - SS_1}{SS_0} \times 100$$

$$\text{filler one pass retention (F-OPR\%)} = \frac{Ash_0 - Ash_1}{Ash_0} \times 100$$

[0098] The obtained results are shown in Table 2.

Table 2

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	T-OPR(%)	F-OPR(%)
	Kind	Dosage (based on SS wt) (ppm)				
1	A	200	300	0	80.6	60.8
2	B	200	300	0	81.2	63.8
3	C	200	300	0	79.9	59.6

Table continued

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	T-OPR(%)	F-OPR(%)
	Kind	Dosage (based on SS wt) (ppm)				
4	D	200	300	0	81.3	64.3
5	E	200	300	0	80.8	62.4
6	F	200	300	0	79.5	58.8
7	A	300	0	500	82.5	63.9
8	B	300	0	500	83.2	66.1
9	C	300		500	81.5	62.1
10	D	300	0	500	83.2	67.9
11	E	300	0	500	82.5	63.2
12	F	300	0	500	81.6	61.1
13	A	300	150	250	83.4	68.7
14	D	300	150	250	83.6	69.9

(Comparative Examples 15 to 28)

[0099] The retention rate was measured in the same manner as in Comparative Examples 1 to 14 using solution polymerization type polymers and emulsion type polymers (a) to (f) in place of the polymer dispersions (A) to (F) used in Comparative Examples 1-14. The obtained results are shown in Table 3. The compositions and properties of the polymers are shown in Table 1.

Table 3

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on weight of SS) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on weight of SS) (ppm)				
15	a	200	300	0	78.3	49.5
16	b	200	300	0	77.3	42.3
17	c	200	300	0	78.0	53.0
18	d	200	300	0	76.8	41.2
19	e	200	300	0	77.7	47.8
20	f	200	300	0	76.5	40.4
21	a	300	0	500	79.3	53.3
22	b	300	0	500	78.4	48.3
23	c	300	0	500	78.6	54.9
24	d	300	0	500	78.5	43.9
25	e	300	0	500	79.3	51.4
26	f	300	0	500	78.5	45.1
27	a	300	150	250	79.3	56.9
28	d	300	150	250	78.9	47.5

(Examples 1 to 16)

[0100] The retention rate was measured in the same manner as in Comparative Examples 1 to 14 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite. The obtained results are shown in Table 4.

Table 4

Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt)(ppm)					
1	A	250	0	150	0	81.8	62.2
2	B	250	0	150	0	82.0	62.0
3	C	250	0	150	0	82.4	62.5
4	D	250	0	150	0	82.5	62.5
5	E	250	0	150	0	82.3	62.2
6	F	250	0	150	0	82.1	62.0
7	A	250	0	0	150	82.3	62.0
8	B	250	0	0	150	82.5	62.5
9	C	250	0	0	150	82.5	62.5
10	D	250	0	0	150	82.3	62.2
11	E	250	0	0	150	82.1	62.0
12	F	250	0	0	150	81.9	62.0
13	A	250	250	80	0	86.0	67.5
14	D	250	250	80	0	85.5	68.5
15	A	250	250	0	80	87.5	67.2
16	D	250	250	0	80	87.5	68.5

(Comparative Examples 29 to 44)

[0101] The retention rate was measured in the same manner as in Comparative Examples 15 to 28 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite. The obtained results are shown in Table 5.

Table 5

Comparative Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)					
29	a	250	0	150	0	76.2	54.2
30	b	250	0	150	0	77.0	54.0
31	c	250	0	150	0	77.5	54.5
32	d	250	0	150	0	77.5	54.5
33	e	250	0	150	0	77.2	54.2

Table continued

Comparative Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)					
34	f	250	0	150	0	77.0	54.0
35	a	250	0	0	150	77.0	54.0
36	b	250	0	0	150	77.5	54.5
37	c	250	0	0	150	77.5	54.5
38	d	250	0	0	150	77.2	54.4
39	e	250	0	0	150	77.0	54.1
40	f	250	0	0	150	76.5	54.0
41	a	250	250	80	0	81.0	60.5
42	d	250	250	80	0	80.5	60.5
43	a	250	250	0	80	82.5	60.2
44	d	250	250	0	80	82.5	60.0

(Comparative Examples 45 to 58)

[0102] A drainage test was conducted by adding ionic polymer dispersions (A) to (F) to paper stuff.

[0103] Mixed pulp prepared from 90 % of recycled pulp from corrugated board and 10 % of recycled pulp from newspaper (C.S.F. = 300) was diluted to a pulp concentration of 1 wt%, to which 3 wt% of a liquid alum was added (based on the weight of pulp) to obtain a pH value of 5.8.

[0104] 300 ml of this slurry was put into a 500-ml beaker and a 0.1 wt% aqueous solution of each of the polymers (A) to (F) obtained in preparation example Nos. 1~6 was added while stirring by a three-one motor at 600 rpm. After 30 seconds, 0.1 wt% anionic colloidal silica and/or 0.1 wt% bentonite were/was added thereto. After another 30 seconds, stirring was stopped and this slurry was transferred to a 1-liter measuring cylinder. City water was added to the slurry to adjust the total amount to 1 liter, the measuring cylinder was turned around three times for mixing, and the resulting slurry was put into a Canadian Standard freeness tester. In accordance with the procedure for the measurement of C.S.F., the amount of drainage coming out of a lateral pipe was measured.

[0105] The obtained results are shown in Table 6.

Table 6

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
45	A	200	200	0	480
46	B	200	200	0	473
47	C	200	200	0	483
48	D	200	200	0	470
49	E	200	200	0	482
50	F	200	200	0	475
51	A	300	0	500	503
52	B	300	0	500	490
53	C	300	0	500	510

Table continued

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
54	D	300	0	500	495
55	E	300	0	500	505
56	F	300	0	500	502
57	A	300	100	300	513
58	D	300	100	300	570

(Comparative Examples 59 to 72)

[0106] The amount of drainage was measured in the same manner as in Comparative Examples 45 to 58 using the ionic polymers (a) to (f) shown in Table 7 in place of the polymer dispersions (A) to (F) used in Comparative Examples 45 to 58.

[0107] The obtained results are shown in Table 7.

Table 7

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
59	a	200	200	0	442
60	b	200	200	0	452
61	c	200	200	0	446
62	d	200	200	0	435
63	e	200	200	0	455
64	f	200	200	0	443
65	a	300	0	500	460
66	b	300	0	500	465
67	c	300	0	500	463
68	d	300	0	500	450
69	e	300	0	500	470
70	f	300	0	500	460
71	a	300	100	300	470
72	d	300	100	300	462

(Examples 17 to 32)

[0108] The amount of drainage was measured in the same manner as in Comparative Examples 45 to 58 using acrylic acid (co) polymers (G) or (H) and/or bentonite in place the anionic colloidal silica and/or bentonite used in Comparative Examples 45 to 58. The obtained results are shown in Table 8.

Table 8

Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt)(ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)				
17	A	.250	0	150	0	478
18	B	250	0	150	0	472
19	C	250	0	150	0	482
20	D	250	0	150	0	478
21	E	250	0	150	0	480
22	F	250	0	150	0	470
23	A	250	0	0	150	476
24	B	250	0	0	150	474
25	C	250	0	0	150	480
26	D	250	0	0	150	480
27	E	250	0	0	150	478
28	F	250	0	0	150	474
29	A	250	250	30	0	513
30	D	250	250	80	0	505
31	A	250	250	0	80	514
32	D	250	250	0	80	506

(Comparative Examples 73 to 88)

[0109] The amount of drainage was measured in the same manner as in Comparative Examples 59 to 72 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite used in Comparative Examples 59 to 72. The obtained results are shown in Table 9.

Table 9

Comparative Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based SS wt) (ppm)				
73	a	250	0	150	0	448
74	b	250	0	150	0	442
75	c	250	0	150	0	442
76	d	250	0	150	0	448
77	e	250	0	150	0	440
78	f	250	0	150	0	444
79	a	250	0	0	150	446
80	b	250	0	0 .	150	444
81	c	250	0	0	150	440
82	d	250	0	0	150	440
83	e	250	0	0	150	446

Table continued

Comparative Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based SS wt) (ppm)				
84	f	250	0	0	150	444
85	a	250	250	80	0	483
86	d	250	250	80	0	475
87	a	250	250	0	80	434
88	d	250	250	0	80	475

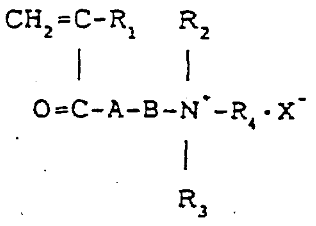
INDUSTRIAL APPLICABILITY

[0110] The papermaking method of the present invention makes it possible to improve fhe retention rates and/or drainage property of cellulose fibers and fillers in the papermaking process, whereby productivity in papermaking and drying steps can be improved. The papermaking method of the present invention also makes it possible to keep clean the circulating white water and reduce a load in the white water recovery step and a load in the waste water treatment step.

Claims

1. A papermaking method comprising the steps of:

adding to paper stuff in a papermaking step an ionic water-soluble polymer obtained by a polymerization method for obtaining a dispersion of fine polymer particles by polymerizing (A) 3 to 100 moil% of a water soluble cationic vinyl monomer represented by the following formula (1):



$$\begin{array}{l} CH_2=C-R_1 \quad\;\; R_2 \\ \quad\;\; | \qquad\quad\;\; | \\ \;\; O=C-A-B-N^{+}-R_4\cdot X^{-} \\ \qquad\qquad\quad\;\; | \\ \qquad\qquad\quad\; R_3 \end{array} \qquad (1)$$

(wherein A is O or NH; B is C_2H_4, C_3H_6 or C_3H_5OH, R_1 is H or CH_3; R_2 and R_3 are each CH_3 or C_2H_5; R_4 is H, CH_3, C_2H_5 or benzyl group; and X^- is an anionic counter ion), or a mixture thereof, (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer; and (C) the remainder consisting of a water-soluble non-ionic vinyl monomer based on the total amount of all monomers under agitation in an aqueous salt solution capable of dissolving the monomers and not the produced polymer in the presence of a dispersant which is composed of a polymer electrolyte soluble in the aqueous salt solution;

mixing said ionic polymer with the paper stuff; and

adding and mixing an anionic additive consisting of organic anionic (co)polymer or a mixture of organic anionic copolymer and anionic colloidal silica and/or bentonite so as to improve retention and/or drainage property.

2. The papermaking method according to claim 1, wherein a salt forming the aqueous salt solution is a divalent anionic salt.

3. The papermaking method according to claims 1 or 2, wherein said dispersant is a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of a cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 0 to 50 mol% of acrylamide.

4. The papermaking method according to any one of claims 1 to 3, wherein said ionic water-soluble polymer has an intrinsic viscosity in a 2 wt% ammonium sulfate aqueous solution of 5 dl/g to 30 dl/g.

5. The papermaking method according to any one of claims 1 to 4, wherein the dosage of said ionic polymer is 0.001 to 0.2 wt% based on the weight of said paper stuff SS and the total dosage of said anionic additive is 0.001 to 0.5 wt% based on the weight of said paper stuff SS.

6. The papermaking method according to claim 5, wherein the dosage of said ionic polymer is 0.001 to 0.05 wt% based on the weight of said paper stuff SS and the total dosage of said anionic additive is 0.01 to 0.2 wt% based on said weight of the paper stuff.

7. The papermaking method according to any one of claims 1 to 6, wherein the anionic additive is an anionic (co) polymer comprising acrylic acid of 15~100 mol% and acrylamide of 0~85 mole % based on the total of all the monomers.

8. The papermaking method according to any one of claims 1 to 7, wherein the anionic additive, which is added after the ionic polymer is added and mixed, is an anionic (co)polymer polymerized in an aqueous salt solution capable of dissolving the monomers but not the produced polymer, and a water-diluted dispersion of the resulted polymer fine particles is added thereto as said anionic (co)polymer.

9. The papermaking method according to any one of claims 1 to 8, wherein said ionic water-soluble polymer is added before the centrifugal screening of the papermaking process and said anionic additive is added after the centrifugal screening.

10. The papermaking method according to any one of claims 1 to 9, wherein said ionic water-soluble polymer contains 1 to 30 mol% of said water-soluble anionic vinyl monomer based on the total of all the monomers.

11. The papermaking method according to claim 10, wherein said anionic monomer is one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, acrylamide-2-methylpropanesulfonic acid and salts thereof, and mixtures thereof.

12. The papermaking method according to claim 11, wherein said anionic monomer is acrylic acid.

13. The papermaking method according to any one of claims 1 to 12, wherein the gram equivalent value of said water-soluble cationic vinyl monomer used in said ionic water-soluble polymer is greater than the gram equivalent value of said water-soluble anionic vinyl monomer.

14. The papermaking method according to any one of claims 1 to 9, wherein said ionic water-soluble polymer does not contain any water-soluble anionic vinyl monomer.

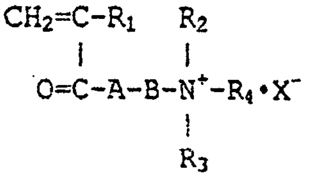
15. The papermaking method according to any one of claims 1 to 14, wherein said water-soluble nonionic vinyl monomer is acrylamide.

16. The papermaking method according to any oneof claims 1 to 15, wherein said water-soluble cationic vinyl monomer is a tertiary salt and/or quaternary product of dimethylaminoethylacrylate.

Patentansprüche

1. Papierherstellungsverfahren, umfassend die Schritte:

Zugabe zu Papierbrei in einer Papierherstellungsstufe eines ionischen wasserlöslichen Polymers, das durch ein Polymerisationsverfahren zum Erhalten einer Dispersion von feinen Polymerteilchen durch Polymerisieren von (A) 3 bis 100 Mol-% eines wasserlöslichen kationischen Vinylmonomers der allgemeinen Formel (1)


(1)

$$CH_2=C(R_1)-C(=O)-A-B-N^+(R_2)(R_3)-R_4\cdot X^- \qquad (1)$$

(worin der Rest A ein O-Atom oder eine NH-Gruppe ist, der Rest B eine C_2H_4-, C_3H_6- oder C_3H_5OH-Gruppe ist, der Rest R_1 ein H-Atom oder eine CH_3-Gruppe ist, die Reste R_2 und R_3 jeweils eine CH_3- oder C_2H_5-Gruppe sind, der Rest R_4 ein H-Atom, eine CH_3-, C_2H_5- oder Benzylgruppe ist und der Rest X- ein anionisches Gegenion ist) oder eines Gemisches davon, (B) 0 bis 30 Mol-% eines wasserlöslichen anionischen Vinylmonomers und (C) eines Rests aus einem wasserlöslichen nicht ionischen Vinylmonomer, basierend auf der Gesamtmenge aller Monomere, unter Rühren in einer wäßrigen Salzlösung, die fähig ist, die Monomere, aber nicht das erzeugte Polymer zu lösen, in Gegenwart eines Dispergiermittels, das aus einem Polymerelektrolyten zusammengesetzt ist, der in der wäßrigen Salzlösung löslich ist, erhalten wird,
Mischen des ionischen Polymers mit dem Papierbrei, und
Zugeben und Mischen eines anionischen Additivs, bestehend aus organischem, anionischem (Co-)Polymer oder einem Gemisch aus organischem, anionischem Copolymer und anionischem kolloidalem Silicamaterial, und/oder Bentonit, um Retentions- und/oder Entwässerungseigenschaften zu verbessern.

2. Papierherstellungsverfahren gemäß Anspruch 1, wobei ein Salz, das die wäßrige Salzlösung bildet, ein zweiwertiges anionisches Salz ist.

3. Papierherstellungsverfahren gemäß Anspruch 1 oder 2, wobei das Dispergiermittel ein kationischer Polymerelektrolyt ist, erhalten durch Polymerisieren von 50 bis 100 Mol-% eines kationischen Monomers, das ausgewählt ist aus Dimethylaminoethylacrylatsalzen, Dimethylaminoethylmethacrylatsalzen, Dimethylaminopropylacrylamidsalzen, Dimethylaminopropylmethacrylamidsalzen, Acryloyloxyethyltrimethylammoniumchlorid, Methacryloyloxyethyltrimethylammoniumchlorid, Acrylamidpropyltrimethylammoniumchlorid, Methacrylamidpropyltrimethylammoniumchlorid, Dimethyldiallylammoniumchlorid und Gemischen davon, und 0 bis 50 Mol-% Acrylamid.

4. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 3, wobei das ionische wasserlösliche Polymer eine innere Viskosität in einer 2 Gew.-%igen wäßrigen Ammoniumsulfatlösung von 5 dl/g bis 30 dl/g hat.

5. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 4, wobei die Dosierung des ionischen Polymers 0,001 bis 0,2 Gew.-%, auf der Basis des Gewichts des Papierbreis SS, und die Gesamtdosierung des anionischen Additivs 0,001 bis 0,5 Gew.-%, auf der Basis des Gewichts des Papierbreis SS, beträgt.

6. Papierherstellungsverfahren gemäß Anspruch 5, wobei die Dosierung des ionischen Polymers 0,001 bis 0,05 Gew.-%, auf der Basis des Gewichts des Papierbreis SS, und die Gesamtdosierung des anionischen Additivs 0,01 bis 0,2 Gew.-%, auf der Basis des Gewichts des Papierbreis SS, beträgt.

7. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 6, wobei das anionische Additiv ein anionisches (Co-)Polymer, umfassend 15 bis 100 Mol-% Acrylsäure und 0 bis 85 Mol-% Acrylamid, auf der Basis aller Monomere, ist.

8. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 7, wobei das anionische Additiv, das nach dem ionischen Polymer zugegeben und gemischt wird, ein anionisches (Co-)Polymer ist, das in einer wäßrigen Salzlösung polymerisiert wird, die die Monomeren, aber nicht das erzeugte Polymer lösen kann, und wobei eine mit Wasser verdünnte Dispersion der erzeugten feinen Polymerteilchen dazu als anionisches (Co-) Polymer gegeben wird.

9. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 8, wobei das ionische wasserlösliche Polymer im Papierherstellungsverfahren vor dem Zentrifugalsichten zugesetzt wird und wobei das anionische Additiv nach dem Zentrifugalsichten zugesetzt wird.

10. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 9, wobei das ionische wasserlösliche Polymer 1 bis 30 Mol-% des wasserlöslichen anionischen Vinylmonomers, auf der Basis aller Monomere, enthält.

11. Papierherstellungsverfahren gemäß Anspruch 10, wobei das anionische Monomer ausgewählt ist aus Acrylsäure und Salzen davon, Methacrylsäure und Salzen davon, Itaconsäure und Salzen davon, Acrylamid-2-methylpropansulfonsäure und Salzen davon und Gemischen davon.

12. Papierherstellungsverfahren gemäß Anspruch 11, wobei das anionische Monomer Acrylsäure ist.

13. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 12, wobei der Grammäquivalentwert des wasserlöslichen kationischen Vinylmonomers, das in dem ionischen wasserlöslichen Polymer verwendet wird, größer ist als der Grammäquivalentwert des wasserlöslichen anionischen Vinylmonomers.

14. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 9, wobei das ionische wasserlösliche Polymer kein wasserlösliches anionisches Vinylmonomer enthält.

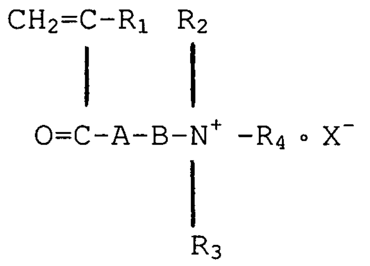
15. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 14, wobei das wasserlösliche nicht ionische Vinylmonomer Acrylamid ist.

16. Papierherstellungsverfahren gemäß einem der Ansprüche 1 bis 15, wobei das wasserlösliche kationische Vinylmonomer ein tertiäres Salz und/oder quaternäres Produkt von Dimethylaminoethylacrylat ist.

Revendications

1. Procédé de fabrication du papier, comprenant les étapes de :

addition à une pâte à papier, dans une étape de fabrication du papier, d'un polymère ionique soluble dans l'eau obtenu par un procédé de polymérisation pour obtenir une dispersion de fines particules de polymère par polymérisation de (A)3 à 100% en moles d'un monomère cationique soluble dans l'eau représenté par la formule (1) suivante:



$$CH_2=C(R_1)-C(=O)-A-B-N^+(R_2)(R_3)-R_4 \circ X^- \qquad (1)$$

(dans laquelle A est O ou NH; B est C_2H_4, C_3H_6 ou C_3 H_5OH ; R_1 est H ou CH_3 ; chacun de R_2 et R_3 est CH_3 ou C_2H_5 ; R_4 est H, CH_3, C_2H_5 ou le groupe benzyle ; et X^- est un contre-ion anionique)
ou d'un mélange de tels monomères (B) 0 à 30% en moles d'un monomère vinylique anionique soluble dans l'eau et (C) pour le reste, un monomère vinylique non-ionique soluble dans l'eau, par rapport à la quantité totale de tous les monomères, sous agitation dans une solution aqueuse de sel capable de dissoudre les monomères et pas le polymère produit en présence d'un dispersant qui est composé d'un électrolyte polymère soluble dans la solution aqueuse de sel ;
mélange dudit polymère ionique avec la pâte à papier ; et
addition et mélange d'un additif anionique constitué par un (co) polymère anionique ou un mélange de copolymère anionique organique et de silice colloïdale anionique et/ou la bentonite de façon à améliorer la propriété de rétention et/ou de drainage.

2. Procédé de fabrication du papier selon la revendication 1, dans lequel un sel formant la solution aqueuse de sel est un sel anionique divalent.

3. Procédé de fabrication du papier selon la revendication 1 ou 2, dans lequel ledit dispersant est un électrolyte polymère cationique obtenu par polymérisation de 50 à 100% en moles d'un monomère cationique choisi parmi les sels d'acrylate de diméthylaminoéthyle, les sels de méthacrylate de diméthylaminoéthyle, les sels de diméthylaminopropylacrylamide, les sels de diméthylaminopropylméthacrylamide, le chlorure d'acryloyloxéthyltriméthylammonium, le chlorure de méthacryloyloxyéthyltriméthylammonium, le chlorure d'acrylamidopropyltrméthylammonium, le chlorure de méthacrylamidopropyltriméthylammodium, le chlorure de diméthyldiallylammonium et leurs mélanges, et de 0 à 50% en moles d'acrylamide.

4. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 3, dans lequel ledit polymère ionique soluble dans l'eau a une viscosité intrinsèque, dans une solution aqueuse à 2% en poids de sulfate d'ammonium, de 5dl/g à 30d1/g.

5. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 4, dans lequel la dose dudit polymère ionique est de 0,001 à 0,2% en poids par rapport au poids de ladite SS de pâte à papier et la dose totale dudit additif anionique est de 0,001 à 0,5% en poids par rapport au poids de ladite SS de pâte à papier.

6. Procédé de fabrication du papier selon la revendication 5, dans lequel la dose dudit polymère ionique est de 0,001 à 0,05% en poids par rapport au poids de ladite SS de pâte à papier et la dose totale dudit additif anionique est de 0,01 à 0,2% en poids par rapport audit poids de la pâte à papier.

7. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 6, dans lequel l'additif anionique est un (co)polymère anionique comprenant 15 à 100% en moles d'acide acrylique et 0 à 85% en moles d'acrylamide, par rapport au total de tous les monomères

8. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 7, dans lequel l'additif anionique, qui est ajouté après addition et mélange du polymère ionique, est un (co)polymère anionique polymérisé dans une solution aqueuse de sel capable de dissoudre les monomères mais pas le polymère produit, et une dispersion diluée dans l'eau des fines particules de polymère en résultant y est ajoutée à titre dudit (copolymère) anionique.

9. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 8, dans lequel ledit polymère ionique soluble dans l'eau est ajouté avant le tamisage par centrifugation du processus de fabrication du papier et ledit additif anionique est ajouté après le tamisage par centrifugation.

10. Procédé de fabrication selon l'une quelconque des revendications 1 à 9, dans lequel ledit polymère ionique soluble dans l'eau contient 1 à 30% en moles dudit monomère vinylique anionique soluble dans l'eau, par rapport au total de tous les monomères

11. Procédé de fabrication du papier selon la revendication 10, dans lequel ledit monomère anionique est l'un choisi parmi l'acide acrylique et ses sels, l'acide méthacrylate et ses sels, l'acide itaconique et ses sels, l'acide acrylamido-2-méthylpropanesulfonique et ses sels, et leurs mélanges.

12. Procédé de fabrication du papier selon la revendication 11, dans lequel ledit monomère anionique est l'acide acrylique.

13. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 12, dans lequel la valeur équivalente en grammes dudit monomère vinylique cationique soluble dans l'eau utilisé dans ledit polymère ionique soluble dans l'eau est supérieure à la valeur équivalente en grammes dudit monomère vinylique anionique soluble dans l'eau.

14. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 9, dans lequel ledit polymère ionique soluble dans l'eau ne contient aucun monomère vinylique anionique soluble dans l'eau.

15. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 14, dans lequel ledit monomère vinylique non-ionique soluble dans l'eau est l'acrylamide.

16. Procédé de fabrication du papier selon l'une quelconque des revendications 1 à 15, dans lequel ledit monomère vinylique cationique soluble dans l'eau est un sel tertiaire et/ou un produit quaternaire d'acrylage de diméthylaminoéthyle.