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54 **PAPERMAKING PROCESS AND PAPERMAKING ADDITIVE.**

57 A papermaking additive comprising: (A) a cationic acrylamide polymer prepared by the reaction of an acrylamide polymer with a hypohalite under an alkaline condition in a temperature range of 50 to 110°C for a short time, and (B) either an anionic inorganic substance or a cationic polyacrylamide prepared by the copolymerization of a cationic monomer such as an acrylic ester or acrylamide derivative, an α,β -unsaturated carboxylic acid or its salt, and acrylamide.

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Technical Field

The present invention relates to a method for papermaking, and more particularly to, a method for papermaking comprising using both a cationic acrylamide polymer obtained by Hofmann decomposition reaction at an elevated temperature for a short time and an anionic inorganic substance or a cationic polyacrylamide produced by copolymerization, and an additive for papermaking comprising a cationic acrylamide polymer produced by Hofmann decomposition reaction and an anionic inorganic substance or a cationic polyacrylamide prepared by copolymerization.

Background Art

Since it has recently become difficult to obtain raw materials for paper, the amount ratio of old papers in pulp raw materials has increased. As a result, there are demanded paper strength improvers capable of imparting higher paper strength. On the other hand, in practical operations there are demanded chemicals capable of improving freeness due to requirement of increasing the pulp dehydration speed and chemicals capable of improving drying property to meet requirement of decreasing the amount of steam to be used.

A Hofmann decomposition reaction product of polyacrylamide (hereinafter referred to as "Hofmann PAM") is a cationic resin having a primary amino group directly bonded to the polymer main chain, and has been conventionally used as a freeness improver and a paper strength improver in a step of papermaking.

A feature of Hofmann PAM resides in the high aggregation power, and it not only improves freeness, but also improves the strength between fibers due to the hydrogen bond of the primary amino group which is also a cationic group.

However, when the Hofmann PAM is used alone, sometimes an effective fixation to pulp fibers can not be attained depending on the papermaking conditions and the feature of the Hofmann PAM can not be fully exhibited.

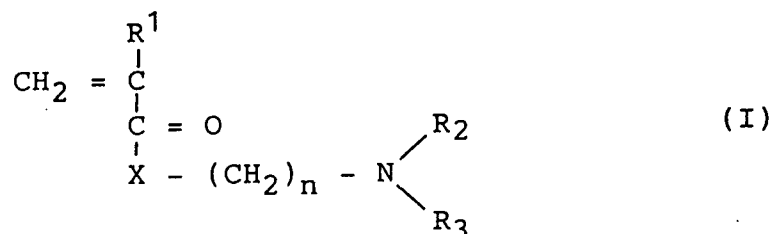
In such a case, problem of freeness can be solved by increasing the amount of Hofmann PAM to be added, but on the other hand, the formation of paper is deteriorated. Therefore, satisfactory results are not always obtained as to paper strength and printing characteristics.

Disclosure of Invention

In view of the above-mentioned points, the present inventors have investigated various additives capable of exhibiting a desirable effect when used together with Hofmann PAM, and as a result, have found that when an anionic inorganic substance or a cationic acrylamide polymer produced by copolymerization is used together therewith, freeness can be controlled without lowering paper strength characteristics, and the present invention has been completed.

That is, the present invention is concerned with a method for papermaking which comprises adding to a pulp slurry a cationic acrylamide polymer produced by reacting an acrylamide polymer with a hypo-halogenite at 50 - 110°C for a short time at an alkaline region and an anionic inorganic substance or a cationic polyacrylamide produced by the copolymerization of

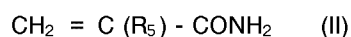
(a) a cationic monomer of the general formula (I)



where R₁ is hydrogen or methyl, R₂ and R₃ are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary ammonium salts produced by the reaction of the compound of the formula (I) with a quaternizing agent,

(b) an α,β-unsaturated carboxylic acid and/or salts thereof, and

(c) an acrylamide monomer of the general formula (II),



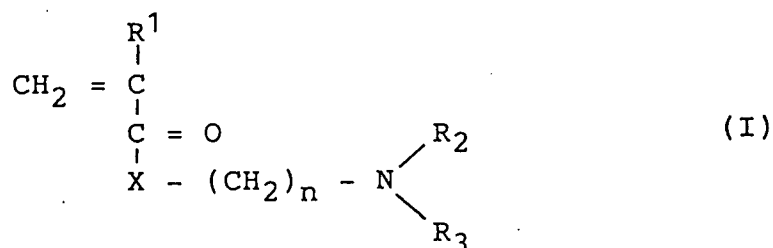
where R_5 is hydrogen or methyl,

and

an additive for papermaking comprising a cationic acrylamide polymer produced by reacting an acrylamide polymer with a hypohalogenite at an alkaline region at 50 - 110 °C for a short time and an anionic inorganic substance or

a cationic polyacrylamide produced by the copolymerization of

(a) a cationic monomer of the general formula (I)

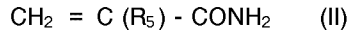


where R_1 is hydrogen or methyl, R_2 and R_3 are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary ammonium salts produced by the reaction of the compound of the formula (I) with a quaternizing agent,

(b) an α,β -unsaturated carboxylic acid and/or salts thereof,

and

(c) an acrylamide monomer of the general formula (II),



where R_5 is hydrogen or methyl.

In the following, the present invention is explained in detail.

The acrylamide polymers used in the present invention include homopolymers of acrylamides (or methacrylamides), copolymers of acrylamides (or methacrylamides) and at least one unsaturated monomer capable of copolymerizing therewith, and further graft copolymers of the acrylamides (or methacrylamides) with water-soluble polymers such as starch and the like.

As the copolymerizable monomers, there may be mentioned hydrophilic monomers, ionic monomers, lipophilic monomers and the like, and at least one monomer may be used.

Concretely the hydrophilic monomers are, for example, diacetone acrylamide,

N,N-dimethylacrylamide,

N,N-dimethylmethacrylamide,

N-ethylmethacrylamide,

N-ethylacrylamide,

N,N-diethylacrylamide,

N-propylacrylamide,

N-acryloylpyrrolidine,

N-acryloylpiperidine,

N-acryloylmorpholine,

hydroxyethyl methacrylate,

hydroxyethyl acrylate,

hydroxypropyl methacrylate,

hydroxypropyl acrylate,

various methoxypolyethylene glycol (meth) acrylates,

N-vinyl-2-pyrrolidone,

and the like.

As ionic monomers, there may be mentioned, for example, acids such as acrylic acid,

methacrylic acid,
vinylsulfonic acid,
allylsulfonic acid,
methallylsulfonic acid,
5 styrene sulfonic acid,
2-acrylamido-2-phenylpropane sulfonic acid,
2-acrylamido-2-methylpropane sulfonic acid,
and the like, and salts thereof,
and

10 amines such as
N,N-dimethylaminoethyl methacrylate,
N,N-diethylaminoethyl methacrylate,
N,N-dimethylaminoethyl acrylate,
N,N-dimethylaminopropyl methacrylamide,
15 N,N-dimethylaminopropyl acrylamide,
and the like, and salts thereof.

As lipophilic monomers, there may be mentioned, for example,
N-alkyl (meth)acrylamide derivatives such as

N,N-di-n-propyl acrylamide,
20 N-n-butyl acrylamide,
N-n-hexyl acrylamide,
N-n-hexyl methacrylamide,
N-n-octyl acrylamide,
N-n-octyl methacrylamide,
25 N-tert-octyl acrylamide,
N-dodecyl acrylamide,
N-n-dodecyl methacrylamide,
and the like,

N-(ω -glycidoxyalkyl) (meth)acrylamide derivatives such as

30 N,N-diglycidyl acrylamide,
N,N-diglycidyl methacrylamide,
N-(4-glycidoxybutyl) acrylamide,
N-(4-glycidoxybutyl) methacrylamide,
N-(5-glycidoxypentyl) acrylamide,
35 N-(6-glycidoxyhexyl) acrylamide,
and the like,

(meth)acrylate derivatives such as

methyl (meth)acrylate,
ethyl (meth)acrylate,
40 butyl (meth)acrylate,
lauryl (meth)acrylate,
2-ethylhexyl (meth)acrylate,
glycidyl (meth)acrylate
and the like,

45 acrylonitrile,
methacrylonitrile,
vinyl acetate,
vinylidene chloride,
olefins such as ethylene, propylene, butene and the like,

50 styrene,
divinyl benzene,
 α -methylstyrene,
butadiene,
isoprene,
55 and the like.

The amount of the unsaturated monomer used for copolymerization varies depending on the types of unsaturated monomers and combination thereof, but is usually 0 - 50 % by weight.

As water-soluble polymers to be used for graft copolymerization with the above-mentioned monomers,

there may be used both natural ones and synthetic ones.

As natural water-soluble polymers, there may be used starches of different origin and modified starches such as oxidized starch, carboxyl starch, dialdehyde starch, cationmodified starch and the like, cellulose derivatives such as methyl cellulose, ethyl cellulose, carboxymethyl cellulose, hydroxyethylcellulose and the like, alginic acid, agar, pectin, carrageenan, dextran, pururan, arum root, Arabia rubber, casein and gelatin.

As synthetic water-soluble polymers, there may be mentioned polyvinyl alcohol, polyvinyl ether, polyvinyl pyrrolidone, polyethylene imine, polyethylene glycol, polypropylene glycol, polymaleic acid copolymer, polyacrylic acid, polyacrylamides and the like.

The amount of the monomer to be added to the above-mentioned water-soluble polymer is 0.1 - 10.0 times the weight of the water-soluble polymer.

Then the above-mentioned monomers are polymerized to prepare polyacrylamide. As the methods for polymerization, free-radical polymerization is preferable, and as the polymerization solvent, polar solvents such as water, alcohols, dimethylformamide and the like are usable, but since Hofmann decomposition reaction is carried out in an aqueous solution. It is preferable to effect the polymerization in an aqueous solution.

The concentration of monomers is such a case as above is 2 - 30 % by weight, preferably 5 - 30 % by weight.

As the polymerization initiator, there is not any limitation as far as it is water-soluble. The polymerization initiator is usually dissolved in an aqueous solution of monomers and used.

Concretely, as peroxide initiators, there may be mentioned, for example, ammonium persulfate, potassium persulfate, hydrogen peroxide, tert-butyl peroxide and the like.

In such a case, the peroxide can be used alone, but may be also used as a redox polymerization agent by combining with a reducing agent.

As the reducing agent, there may be used, for example, sulfites, hydrogen sulfites, salts of low order ionization metals such as iron, copper, cobalt and the like, organic amines such as N,N,N',N'-tetramethyl ethylenediamine and the like, and reducing sugars such as aldose, ketose and the like.

As azo compounds, there may be used 2,2'-azobis-2-amidinopropane hydrochloride, 2,2'-azobis-2,4-dimethylvaleronitrile, 4,4'-azobis-4-cyanovaleric acid, salts thereof and the like.

Further, two or more of the above-mentioned polymerization initiator may be used in combination.

When graft polymerization is effected to a water soluble polymer, other than the above-mentioned polymerization initiator, there may be also used transition metal ions such as ceric ion, ferric ion and the like, and further, such ions may be used in combination with the above-mentioned polymerization initiators.

The amount of the initiator to be added may be 0.01 - 10 % by weight based on the weight of monomers, preferably 0.02 - 8 % by weight. In the case of a redox initiator, the amount of the reducing agent to be added may be 0.1 - 100 %, preferably 0.2 - 80 % based on the initiator in terms of mole.

The polymerization temperature is as low as 30 to 90 °C in the case of a single polymerization initiator, and much lower such as about -5 to 50 °C in the case of a redox polymerization initiator.

In addition, it is not necessary to keep the temperature at a constant temperature, and the temperature may be changed accordingly as the polymerization proceeds. In general, as the polymerization proceeds, the temperature rises due to the generated polymerization heat.

The atmosphere in the polymerization vessel at that time is not particularly limited, but it is desirable to replace the atmosphere with an inert gas such as nitrogen gas for the purpose of accelerating the polymerization. The polymerization time is not critical, but is usually 1 - 20 hours.

Then, the polyacrylamide produced by the above-mentioned method is subjected to Hofmann decomposition reaction. When the polyacrylamide as a starting material is prepared in an aqueous solution, it can be directly used or, if necessary, it is diluted and then used for the reaction.

In the case of graft copolymerization, there is produced polyacrylamide not grafted as a by-product, but the product is directly used for the reaction without removing the non-grafted one.

Hofmann decomposition reaction is effected by acting a hypohalogenite on the amido group of polyacrylamide in the presence of an alkaline substance.

As a hypohalogenous acid, there may be mentioned hypochlorous acid, hypobromous acid, and hypoiodous acid.

As a hypohalogenite, there may be used metal or alkaline earth metal salts. Concretely, they may be sodium hypochlorite, potassium hydrochlorite, lithium hypochlorite, calcium hypochlorite, magnesium hypochlorite, barium hypochlorite and the like. Similarly, there may be mentioned alkali metal or alkaline earth metal hypobromite and hypoiodite in case of hypobromite and hypoiodite.

It is also possible to produce hypohalogenite by blowing a halogen gas into an alkaline solution.

On the other hand, as alkaline substances, there may be mentioned alkali metal hydroxide, alkaline

earth metal hydroxide, alkali metal carbonate and the like.

Among them, alkali metal hydroxides are preferable, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide and the like are mentioned.

The amount of the above-mentioned substance to be added to polyacrylamides is 0.05 - 2.0 mol, preferably 0.1 - 1.5 mol per amido group in the case of hypohalogenous acid, 0.05 - 4.0 mol, preferably 0.1 - 3.0 mol per amido group in the case of alkaline substance. The pH in such a case is usually 11 - 14.

The concentration of polyacrylamide in such a case is usually 0.1 - 17.5 % by weight, but preferably 0.1 - 10 % by weight since a high reaction concentration results in difficult agitation or causes gelation.

Further, when the reaction concentration is less than 1 %, the reaction speed becomes so slow that it is more preferable that the reaction concentration is 1 - 10 % by weight. The reaction temperature may be 50 - 110°C, preferably 60 - 100°C. The Hofmann decomposition reaction is carried out at the above-mentioned temperature range within a short time. The reaction time varies depending on reaction temperature and polymer concentration in the reaction solution, and therefore, the reaction time can not be definitely mentioned, but, for example, when the polymer concentration is 1 % by weight, it is within ten and several minutes at 50°C and within several minutes at 65°C and sufficiently within several tens sec. at 80°C. Further, when the polymer concentration is high, the reaction time can be shorter.

The relation between the reaction time and the reaction temperature may be generally within the range defined by the following two formulas, and when the reaction is carried out within such range, a good result can be obtained,

$$t \text{ (sec)} \geq e^{\frac{15,150}{273+T}} \times 2.5 \times 10^{-20} \quad (1)$$

$$t \text{ (sec)} \leq e^{\frac{15,150}{273+T}} \times 10^{-18} + 30 \quad (2)$$

T : Reaction temperature (°C)

$$50 \leq T \leq 110$$

Cationic polyacrylamides produced under the above-mentioned conditions have a cation equivalent determined by colloid titration at pH 2 of about 0 - 10.0 meq/g, and said cation equivalent can be controlled by the amount of hypohalogenite added.

Since the reaction is carried out in an alkaline region, the amino group is hydrolyzed to produce carboxyl group as a by-product. The amount of the by-production is about 0 - 10.0 meq/g in terms of anion equivalent measured by colloid titration at pH 10. The amount of by-production can be controlled by adjusting the amount of the alkaline substance added.

After effecting the reaction under the above-mentioned conditions, it is preferable to stop the reaction so as to suppress the proceeding of a side-reaction. However, when the product is used immediately after the reaction, sometimes it is not necessary to stop the reaction.

The procedure of stopping the reaction may be (1) adding a reducing agent, (2) cooling, (3) lowering the pH of the solution by adding an acid, or the like. These procedures may be used alone or in combination. (1) is a method for deactivating the remaining hypohalogenite and the like by the reaction with a reducing agent.

In general, when the Hofmann decomposition reaction has completed, there still remain compounds having active chlorine such as unreacted hypohalogenites and the like. When such a reaction solution is used as a paper strength agent, it causes rust on paper-making machines, and therefore, usually the active chlorine is deactivated by using a reducing agent.

However, when a hypohalogenite is reacted in an amount of equivalent mol. or less based on mol. of acrylamide unit of the polymer and at a high temperature, after completion of the reaction, unreacted hypohalogenite hardly remains.

Therefore, the product can be used as a paper strength agent without deactivating active chlorine by using a reducing agent.

(2) is concerned with a method for suppressing the proceeding of reaction. As a procedure thereof,

there may be cooling with heat exchanger, diluting with cold water and the like. The temperature is usually 50° C or less, preferably 45° C or less more preferably 40° C or less.

According to (3), Hofmann decomposition reaction is stopped by lowering the pH of the solution after completion of the reaction which is usually alkaline such as pH 12 - 13 by using an acid and the progress of hydrolysis reaction is simultaneously suppressed.

At that point, it is necessary only that the pH is neutral or less, preferably 4 - 6.

A reaction stopping method may be appropriately selected from (1) - (3) depending on the reaction conditions, and the methods may be used in combination.

Anionic inorganic substances which can be used together with Hofmann decomposition PAM produced by the above-mentioned method may be sodium silicate, anionic particule-like inorganic substances and mixtures thereof.

Sodium silicate can be produced by melting silicon dioxide with sodium carbonate or sodium hydroxide at an elevated temperature, and commercially available water glass also may be used. The structure is shown by the following general formula:



where n is 1 - 4. The examples are sodium metasilicate, sodium orthosilicate, No. 1, No. 2 and No. 3 water glasses and the like.

The form to be used may be such that flake or powder thereof or the like is dissolved in water, or commercially available aqueous solution products also may be used.

As an anionic particle-like inorganic substance, it is necessary only that it is not soluble in water and is anionically charged in water, and various materials can be used.

Concretely, the examples may be silicon dioxide, aluminum oxide, antimony oxide, titanium oxide, and oxides such as clay minerals, for example, aluminosilicates such as montmorillonite, bentonite, kaolin, activated clay, silica sand, diatomaceous earth and the like, magnesiasilicates such as talc, and further carbonates such as calcium carbonate and the like.

When the size of the above-mentioned particles is too large, the composite effect becomes small. The particle size is usually 100 μm or less, preferably 50 μm or less, more preferably 10 μm or less.

The ratio of anionic inorganic substance to Hofmann decomposition PAM when both are added may be such that the amount of anionic inorganic substance is 1 - 500 % by weight, preferably 2 - 400 % by weight, more preferably 3 - 300 % by weight based on Hofmann decomposition PAM. When the ratio is too small, the effect due to the combined use is not obtained while when it is too large, the function of Hofmann decomposition PAM is deteriorated.

The Hofmann decomposition rate is not particularly critical, but usually 5 - 60 mol %, preferably 10 - 50 mol %.

A practical procedure for adding anionic inorganic substances in combination with Hofmann decomposition PAM is such that Hofmann decomposition PAM used in the present invention is produced by the reaction at a high temperature for a short time and the product can be directly used, and since the resulting reaction fluid is strongly alkaline, the combined addition may be effected by any procedure.

Concretely, (i) upon effecting Hofmann decomposition reaction, the anionic inorganic substance is added to and dissolved in sodium hydroxide, sodium hypochlorite or mixture solutions thereof in advance and the mixture is used for Hofmann decomposition reaction.

(ii) After Hofmann decomposition reaction, the anionic inorganic substance is added to the reaction fluid.

(iii) Both are added separately.

The amount of Hofmann decomposition PAM and anionic inorganic substance added to pulp is usually 0.005 - 5.0 %, preferably 0.01 - 2.0 % based on the dry weight of pulp.

In such a case, the ratio of Hofmann decomposition PAM to anionic inorganic substance varies depending on papermaking conditions. Concretely, for example, when it is intended to increase freeness so as to accelerate the papermaking speed, the ratio of anionic inorganic substance is rendered small while when it is intended to control the formation and make uniform paper, the ratio of anionic inorganic substance is increased.

According to the process of the present invention, sometimes the effect is further enhanced when aluminum sulfate or water-soluble anionic resins is used in combination.

The water-soluble anionic resins used here may be water-soluble resins having an anionic substituent such as carboxyl group, sulfonic acid group, phosphoric acid group and the like, or salts thereof.

Examples of said resins are :
anionic acrylamide resins,

anionic polyvinyl alcohol resins,
 carboxymethylcellulose,
 carboxymethylated starch,
 sodium alginate, and the like.

5 The point when the addition is effected is not critical, that is, the addition may be effected before or after Hofmann decomposition PAM and sodium silicate are added to a pulp slurry, or simultaneously. Further, the addition may be effected to each of Hofmann decomposition PAM and sodium silicate or to a mixture solution thereof.

The place where the addition is effected may be anywhere as far as it is before forming a wet sheet.

10 It is preferable to add to a place where chemicals can be sufficiently mixed with and diluted with the pulp slurry and which is near the papermaking wire part, for example, machine chest, mixing box, seed box, white water pit, outlet of screen and the like.

As a papermaking machine, there may be used either Fourdrinier paper machine or cylinder paper machine.

15 After the present additive for papermaking is added to a pulp slurry having a concentration of 0.5 - 5.0 %, a pH 4.0 - 9.0 at a temperature of 20 - 70 °C, a wet sheet is formed at a wire part and then water is squeezed at a press part. The nip pressure at the press part ranges from 20 to 400 kg/cm. After passing the press part, the wet sheet is transferred to a dry part and dried with steam.

20 The steam pressure is 2 - 15 kg/cm² and the drying is carried out in a drum at 80 - 200 °C. After this process, chemical treatments may be effected at a size press or calender so as to improve printing property, surface strength, water resistance, and water repellency.

The additive for papermaking in the present invention comprising a Hofmann decomposition PAM and an anionic inorganic substance as effective components. The concentration of the effective components may be 0.001 - 50 %.

25 The amount ratio of anionic inorganic substance to Hofmann decomposition PAM may be 1 - 500 % by weight, preferably 2 - 400 %, more preferably 3 - 300 %. When the mixing ratio is too low, the mixing effect due to the mixing is not obtained while when the ratio is too high, the property of the Hofmann PAM is deteriorated. The Hofmann decomposition rate here is not particularly critical, but usually 5 - 60 mol %, preferably 10 - 50 mol %.

30 As a procedure for mixing a Hofmann decomposition PAM and an anionic inorganic substance, (i) upon carrying out Hofmann decomposition reaction, they may be added to or dissolved in sodium hydroxide, sodium hypochlorite or a mixture solution thereof in advance and the resulting mixture is used for the Hofmann decomposition reaction.

(ii) After Hofmann decomposition reaction, they may be mixed with the resulting reaction fluid.

35 The solution after the Hofmann decomposition reaction is usually of pH 12 - 13, but the pH may be lowered with an inorganic or organic acid before it is mixed with an anionic inorganic substance, and further, it is possible to lower the pH after mixing with an anionic inorganic substance. The additive for papermaking of the present invention may have pH 2 - 14.

40 According to the present invention, the cationic monomers of the general formula (I) as above are, for example, (meth)acrylic acid ester derivatives represented by dimethylaminoethyl (meth)acrylate and diethylaminoethyl (meth)acrylate, and (meth)acrylamide derivatives represented by dimethylaminopropyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide.

The organic or inorganic acid salts may be salts of inorganic acids such as sulfuric acid, hydrochloric acid, phosphoric acid and the like, or salts of organic acids such as acetic acid, formic acid and the like.

45 As quaternary ammonium salts obtained by the reaction of the compound of the general formula (I) above with a quaternizing agent, there may be mentioned, for example, vinyl monomers having a quaternary ammonium salt produced by the reaction of a vinyl monomer having a tertiary amino group with a quaternizing agent such as methyl chloride, methyl bromide, methyl iodide, dimethyl sulfuric acid, epichlorohydrin, benzyl chloride and the like.

50 According to the present invention, a vinyl monomer having a tertiary amino group, or organic or inorganic salts thereof may be used in combination with a quaternary ammonium salts obtained by the reaction with a quaternizing agent. The mixing ratio of these components is not critical.

The amount of the cationic monomer is usually 0.5 - 70 mol %, preferably 2 - 50 mol %.

55 The α,β -unsaturated carboxylic acids or salts thereof, for example, alkali metal salts or ammonium salt thereof are vinyl monomers having anionicity, for example, unsaturated carboxylic acids such as maleic acid, fumaric acid, itaconic acid,

(meth)acrylic acid,
crotonic acid,
citraconic acid,
and the like,

5 and alkali metal salts thereof such as sodium salts, potassium salts and the like, and ammonium salts thereof.

The amount of the monomer may be 0.5 - 20 mol %, preferably 2 - 20 mol %.

The monomer represented by the general formula (II) of the present invention may be acrylamide and methacrylamide, and commercially available such monomers in the form of powder or an aqueous solution
10 may be sufficiently used. The amount of the monomer used may be 10 - 90 mol %.

According to the present invention, as a fourth component other than (a) - (c), there may be used a crosslinking monomer (d).

The crosslinking monomer may be a monomer having at least two double bonds in the molecule and an N-alkoxymethyl (meth)acrylamide derivative.

15 Concretely, examples of the former include

methylene bisacrylamide,
diallyl acrylamide,
triacrylformal,
diacryloylimide,
20 ethylene glycol acrylate,
ethylene glycol dimethacrylate,
propylene glycol diacrylate
1,3-butylene glycol dimethacrylate,
1,4-butylene glycol methacrylate,
25 glycerol dimethacrylate,
neopentyl glycol dimethacrylate,
trimethylol propane triacrylate,
divinylbenzene,
diallyl phthalate,
30 and the like.

The N-alkoxymethyl (meth)acrylamide derivatives include N-hydroxymethyl (meth)acrylamide, for example,

N-methylol (meth)acrylamide,
N-methoxymethyl (meth)acrylamide,
35 N-ethoxymethyl (meth)acrylamide,
N-n-butoxymethyl (meth)acrylamide,
N-tert-butoxymethyl (meth)acrylamide,
and the like.

The amount of the crosslinking agent varies depending on the type of crosslinking monomer, but is
40 usually 0.0001 - 20 mol %, preferably 0.001 - 10 mol %.

When the amount is less than 0.0001 mol %, the paper strength effect can not be sufficiently exhibited. On the contrary, when the amount exceeds 20 mol %, gelation is liable to occur.

As methods for obtaining the cationic polyacrylamide (B) of the present invention, there may be used conventional methods for polymerizing such type of water-soluble vinyl monomers.

45 For example, free-radical polymerization is preferable.

The concentration of the monomer may be 2 - 30 % by weight, preferably 5 - 30 % by weight.

The polymerization initiator is not particularly critical as far as it is water-soluble, and is usually used by dissolving it in an aqueous solution of the monomer.

Examples of polymerization initiators are peroxides such as hydrogen peroxide, benzoyl peroxide and
50 the like; persulfates such as sodium persulfate, potassium persulfate, ammonium persulfate and the like,
bromates such as sodium bromate, potassium bromate and the like,
perborates such as sodium perborate, potassium perborate, ammonium perborate, and the like;
percarbonates such as sodium percarbonate, potassium percarbonate, ammonium percarbonate and the
like;

55 perphosphates such as sodium perphosphate, potassium perphosphate, ammonium perphosphate, and the like; tert-butyl peroxide and the like.

The above-mentioned initiators may be used alone or in combination with a reducing agent as a redox type polymerization agent.

As the reducing agent, there may be mentioned, for example, sulfites, hydrogensulfites, salts of iron, copper, cobalt and the like of a low order ionization, organic amines such as N,N,N',N'-tetramethyl ethylenediamine and the like, and reducing sugars such as aldose and ketose.

As azo compounds, there may be used 2,2'-azobis-4-amidinopropane hydrochloride, 2,2'-azobis-2,4-dimethylvaleronitrile, 4,4'-azobis-4-cyanovaleric acid, salts thereof and the like.

Further, two or more of the above-mentioned polymerization initiator may be used in combination.

The polymerization temperature is as low as 30 to 90 °C in the case of a single polymerization initiator, and much lower such as about 5 to 50 °C in the case of a redox polymerization initiator.

In addition, it is not necessary to keep the temperature at a constant temperature, and the temperature may be changed accordingly as the polymerization proceeds. In general, as the polymerization proceeds, the temperature rises due to the generated polymerization heat.

The atmosphere in the polymerization vessel at that time is not particularly limited, but it is desirable to replace the atmosphere with an inert gas such as nitrogen gas for the purpose of accelerating the polymerization. The polymerization time is not critical, but is usually 1 - 20 hours.

The method of the present invention is used for making paper from pulp, and is effective to improve remarkably freeness for draining water upon papermaking and improve paper strength serving to enhance the mechanical strength of paper.

The amount ratio of Hofmann decomposition PAM and cationic polyacrylamide (B) is optional depending on pulp raw material and white water. However, from the standpoint of mixing effect, it may range from 95 : 5 to 5 : 95, preferably from 80 : 20 to 20 : 80.

The cationic polyacrylamide may be added to pulp in such a manner that Hofmann decomposition PAM and cationic polyacrylamide (B) are separately added to pulp slurry, or Hofmann decomposition PAM and cationic polyacrylamide (B) are firstly mixed and then added to pulp slurry. Either may be used.

In combination of Hofmann decomposition PAM and cationic polyacrylamide (B), sometimes the effect is further enhanced when aluminum sulfate or water-soluble anionic resins is used in combination.

The water-soluble anionic resins used here may be water-soluble resins having an anionic substituent such as carboxyl group, sulfonic acid group, phosphoric acid group and the like, or salts thereof.

Examples of said resins are:

anionic acrylamide resins,
anionic polyvinyl alcohol resins,
carboxymethylcellulose,
carboxymethylated starch,
sodium alginate, and the like.

The point where the agents are to be added is not particularly critical. The agents may be added before or after or simultaneously with adding Hofmann decomposition PAM and cationic polyacrylamide (B) to pulp slurry. Further, the agents may be mixed separately with each of Hofmann decomposition PAM and cationic polyacrylamide (B), or may be mixed with a mixture solution of Hofmann decomposition PAM and cationic polyacrylamide (B).

The place where the addition is effected may be anywhere as far as it is before forming a wet sheet.

It is preferable to add to a place where chemicals can be sufficiently mixed with and diluted with the pulp slurry and which is near the papermaking wire part, for example, machine chest, mixing box, seed box, white water pit, outlet of screen and the like.

As a papermaking machine, there may be used either Fourdrinier paper machine or cylinder paper machine.

After the present additive for papermaking is added to a pulp slurry having a concentration of 0.5 - 5.0 %, pH 4.0 - 9.0 at a temperature of 20 - 70 °C, a wet sheet is formed at a wire part and then water is squeezed at a press part. The nip pressure at the press part ranges from 20 to 400 kg/cm. After passing the press part, the wet sheet is transferred to a dry part and dried with steam.

The steam pressure is 2 - 15 kg/cm² and the drying is carried out in a drum at 80 - 200 °C.

After this process, chemical treatments may be effected at a size press or calender so as to improve printing property, surface strength, water resistance, and water repellency.

The additives for papermaking according to the present invention may be in the form of a water-soluble liquid mixture comprising Hofmann decomposition PAM and cationic polyacrylamide (B) as active components. The concentration of the active components may range from 0.001 to 50 %.

The amount ratio of Hofmann decomposition PAM to cationic polyacrylamide (B) may range, in terms of weight, from 95 : 5 to 5 : 95, preferably from 80 : 20 to 20 : 80.

When the mixing ratio is too small, the effect due to using in combination is not obtained. On the contrary, when the mixing ratio is too large, the function of the Hofmann decomposition PAM is deteriorated.

Here, the decomposition rate of Hofmann decomposition is not particularly critical, but is usually 5 - 60 mol %, preferably 10 - 50 mol %.

A method for mixing Hofmann decomposition PAM and cationic polyacrylamide (B) may be as shown below. The solution after Hofmann decomposition reaction is usually of pH 12 - 13, but the pH may be lowered with an inorganic or organic acid before or after mixing with cationic polyacrylamide (B).

The additives for papermaking according to the present invention may range from 2 to 14.

When paper is manufactured by the above-mentioned method, freeness can be improved without deteriorating paper strength such as rupture strength, internal bond strength, compression strength and the like.

Therefore, when the method of the present invention is used for manufacturing paper products where the content of waste paper in the raw materials is high, such as corrugated board, newspaper and the like, very good results are obtained and paper of high strength can be produced.

Other than corrugated board and newspaper, when the present invention is applied to manufacturing of high strength paper or the case where excellent freeness is required at a papermaking step, there can be produced papers of high strength in a good productivity.

Best Mode for Carrying Out the Invention

The present invention is explained referring to the following examples, but is not restricted by the examples. The "%" in the following is "% by weight" unless otherwise specified.

PREPARATION EXAMPLE 1

24.0 g of a 10 wt. % aqueous polyacrylamide solution (Brookfield viscosity at 25° C : 3,400 cps) was placed in a 500 ml beaker, diluted with 36.0 g of distilled water, and heated to 80° C with stirring, and to the resulting solution was added 14.8 g of a mixture solution of sodium hypochlorite and NaOH (concentration of sodium hypochlorite : 1.0 mol/kg; concentration of NaOH : 2.0 mol/kg). The reaction was stopped 15 sec. after the addition of the above-mentioned mixture solution, and there was obtained a 1 wt. % acrylamide polymer (Hofmann PAM (A)).

A part of the reaction product was added to an aqueous solution of pH 2 and a colloid titration by means of a 1/400 N aqueous solution of potassium polyvinyl sulfonate using toluidine blue as indicator. The resulting cationicity was 4.4 meq./g.

In the following tests the Hofmann PAM (A) was used immediately after the preparation.

PREPARATION EXAMPLE 2

24.0 g of a 12.5 wt. % aqueous polyacrylamide solution (Brookfield viscosity at 25° C : 12,400 cp) was placed in a 500 ml beaker, diluted with 36.0 g of distilled water, and to the resulting solution was added with stirring at 20° C 14.8 g of a mixture solution of sodium hypochlorite and NaOH (concentration of sodium hypochlorite : 1.0 mol/kg; concentration of NaOH : 2.0 mol/kg). Two hours later, 225.2 g of a 0.001 % aqueous solution of sodium sulfite was added thereto to stop the reaction and a 1 wt. % acrylamide polymer (hereinafter called "Hofmann PAM (B)").

A part of the reaction product was added to an aqueous solution of pH 2 and a colloid titration was carried out using a 1/400 N aqueous solution of potassium polyvinyl sulfonate with toluidine blue as indicator and the cationicity was 4.4 meq./g.

EXAMPLE 1

To a pulp slurry (concentration of 1.0 %) having Canadian Standard Freeness (hereinafter called "CSF") of 450 ml and 1.0% concentration obtained from waste paper of corrugated board was added a commercially available rosin emulsion sizing agent in an amount of 0.15% based on the dry weight of pulp followed by stirring for two minutes.

Then, aluminum sulfate was added thereto in an amount of 1.0 % based on the dry weight and then stirring was effected for one minute. The pH of the resulting pulp slurry was 5.1.

Then, No. 3 water glass was added thereto in an amount of 0.30 % based on the dry weight of pulp, and stirring was effected for one minute. Hofmann PAM (A) obtained in Preparation Example 1 was added in an amount of 0.60 % based on the dry weight of pulp, and stirring was continued for further one minute.

Part of the resulting pulp slurry was taken to measure CSF according to JIS-P-8121, and the remainder

was used to make paper in a TAPPI square sheet machine, and then the resulting paper was dried for two hours at 110°C by a hot air blowing dryer to obtain a hand-made paper with a basis weight of 150 ± 3 g/m².

To evaluate the resulting hand-made paper, its "specific compression strength" was measured according to JIS-P-8126, its "specific rupture strength" according to JIS-P-8112 and its "internal bond strength" by a Kumagaya Riki Internal Bond Tester. Table 1 shows the result.

EXAMPLE 2

The procedure of Example 1 was repeated to effect the hand-making paper test except that No. 3 water glass was added in an amount of 0.60 % based on the dry weight. Table 1 shows the result.

EXAMPLE 3

The procedure of Example 1 was repeated to effect the hand-making paper test except that No. 3 water glass was added in an amount of 0.90 % based on the dry weight. Table 1 shows the result.

EXAMPLE 4

The procedure of Example 1 was repeated to effect the hand-making paper test except that No. 3 water glass was added in an amount of 1.50 % based on the dry weight. Table 1 shows the result.

COMPARISON EXAMPLE 1

The procedure of Example 1 was repeated to effect the hand-making paper test except that No. 3 water glass was added in an amount of 0.003 % based on the dry weight. Table 1 shows the result.

COMPARISON EXAMPLE 2

The procedure of Example 1 was repeated to effect the hand-making paper test except that No. 3 water glass was added in an amount of 5.00 % based on the dry weight. Table 1 shows the result.

COMPARISON EXAMPLES 3 and 4

The procedures of Comparison Examples 2 and 4 were repeated respectively except that Hofmann PAM (B) was used in place of Hofmann PAM (A) used in Comparison Examples 1 and 2. Table 1 shows the results.

EXAMPLE 5

To a pulp slurry of Canadian Standard Freeness (hereinafter called "CSF") of 543 ml and 1.0 % concentration obtained from waste paper of corrugated board was added aluminum sulfate in an amount of 0.5 % based on the dry weight of pulp, and stirring was effected for a further minute. The pH of the pulp slurry was 5.8.

Then, colloidal silica (Snowtex 40, particle size 10 - 20 nm, manufactured by Nissan Kagaku K.K.) was added thereto in an amount of 0.25 % based on the dry weight of pulp followed by stirring for 30 sec, and Hofmann PAM (A) obtained in Preparation Example 1 was added thereto in an amount of 1.50 % based on the dry weight of pulp. The stirring was continued for further 30 sec.

A part of the resulting pulp slurry was taken to measure CSF according to JIS-P-8121, and the remainder was used to make paper in a TAPPI square sheet machine. The product was then dried by a hot air blowing dryer at 110°C for two hours to produce a hand-made paper with a basis weight of 150 ± 3 g/m².

To evaluate the resulting hand-made paper, the specific compression strength was measured according to JIS-P-8126, the specific rupture strength according to JIS-P-8112, and the internal bond strength by a Kumagaya Riki Internal Bond Tester. Table 2 shows the result.

EXAMPLE 6

The procedure of Example 5 was repeated to effect the hand-making paper test except that colloidal silica was added in an amount of 0.50 % based on the dry weight.
Table 2 shows the result.

5 EXAMPLE 7

The procedure of Example 5 was repeated to effect the hand-making paper test except that colloidal silica was added in an amount of 1.00 % based on the dry weight.
Table 2 shows the result.

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COMPARISON EXAMPLE 5

The procedure of Example 5 was repeated to effect the hand-making paper test except that colloidal silica was added in an amount of 0.001 % based on the dry weight.

15 Table 2 shows the result.

COMPARISON EXAMPLE 6

The procedure of Example 5 was repeated to effect the hand-making paper test except that colloidal silica was added in an amount of 10.0 % based on the dry weight.

20

Table 2 shows the result.

PREPARATION EXAMPLE 3

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In a four-necked flask equipped with stirrer, reflux condenser, thermometer, and nitrogen inlet pipe were placed 675 g (94 mol %) of 40 % acrylamide, 23.1 % (4 mol %) of dimethylaminoethyl methacrylate, 5.8 g (2 mol %) of acrylic acid, 62.3 mg (0.01 mol %) of bismethylene acrylamide and 1.004 g of water, and the pH of the resulting mixture was adjusted to 4.5 with a 10 % aqueous solution of sulfuric acid. Then the inner temperature was raised to 40 °C while blowing nitrogen gas thereinto. A 10% aqueous solution of ammonium persulfate and a 10% aqueous solution of sodium hydrogen sulfite were added to the above-mentioned mixture with stirring and polymerization was initiated.

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Then, the reaction mixture was kept at 85 °C, and three hours after the beginning of the polymerization, water was added to stop the polymerization reaction and there was obtained a stable aqueous solution of acrylamide polymer having 15.3 % of non-volatile matter, Brookfield viscosity of 6,800 cps at 25 °C and pH 4.3.

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PREPARATION EXAMPLE 4

30.0 g of a 10 wt. % aqueous solution of polyacrylamide (Brookfield viscosity at 25 °C : 3,400 cp) was placed in a 500 ml beaker, diluted with distilled water, heated to 80 °C with stirring, and then 14.3 g of a mixture solution of sodium hypochlorite and NaOH (concentration of sodium hypochlorite : 1.0 mol/kg; concentration of NaOH : 2.0 mol/kg) was added to the resulting solution and 15 sec. later, 225.7 g of cold water at 5 °C was added to stop the reaction. As a result, a 1 wt. % acrylamide polymer (Hofmann PAM (C)) was obtained.

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A part of the reaction product was added to an aqueous solution of pH 2 and a colloid titration was then carried out using a 1/400 N aqueous solution of potassium polyvinyl sulfonate with toluidine blue as indicator and the cationicity was 3.8 meq./g.

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In the following test, Hofmann PAM (C) was used immediately after the preparation.

50 EXAMPLE 8

To a pulp slurry of Canadian Standard Freeness (hereinafter called "CSF") of 400 ml and 1.0 % concentration obtained from waste paper of corrugated board was added a commercially available rosin emulsion sizing agent in an amount of 0.15 % based of the dry weight of pulp followed by stirring for two minutes.

55

Then, aluminum sulfate was added to the resulting mixture in an amount of 1.0 % based on the dry weight of pulp and stirring was effected for a further minute. At this time, the pH of the pulp slurry was 5.1.

Further, the acrylamide polymer obtained in Preparation Example 3 was added to the resulting mixture

as above in an amount of 0.30 % based on the dry weight of pulp. Stirring was effected for one minute and then Hofmann PAM (C) obtained in Preparation Example 4 was added thereto in an amount of 0.10 % based on the dry weight of pulp.

The stirring was continued for a further one minute and then a part of the resulting pulp slurry was taken to measure CSF according to JIS-P-8121, and the remainder was used to make paper in a TAPPI square sheet machine. The resulting product was dried by a hot air blowing dryer at 110 °C for 2 hours to obtain a hand-made paper with a basis weight of 125 ± 3 g/m².

To evaluate the hand-made paper, the specific compression strength was measured according to JIS-P-8126, the specific rupture strength according to JIS-P-8112 and the internal bond strength by a Kumagaya Riki Internal Bond Tester. Table 3 shows the result.

EXAMPLE 9

The procedure of Example 8 was repeated to effect the hand-making paper test except that the polyacrylamide polymer obtained in Preparation Example 3 was added in an amount of 0.20 % based on the dry weight and Hofmann PAM (C) obtained in Preparation Example 4 was added in an amount of 0.20 % based on the dry weight. Table 3 shows the result.

EXAMPLE 10

The procedure of Example 8 was repeated to effect the hand-making paper test except that the polyacrylamide polymer obtained in Preparation Example 3 was added in an amount of 0.10 % based on the dry weight and Hofmann PAM (C) obtained in Preparation Example 4 was added in an amount of 0.30 % based on the dry weight. Table 3 shows the result.

COMPARISON EXAMPLE 7

The procedure of Example 8 was repeated to effect the test except that the acrylamide polymer obtained in Preparation Example 3 was added in an amount of 0.40 % based on the dry weight and Hofmann PAM (C) obtained in Preparation Example 4 was not added. Table 3 shows the result.

COMPARISON EXAMPLE 8

The procedure of Example 8 was repeated to effect the test except that Hofmann PAM (C) obtained in Preparation Example 4 was added in an amount of 0.40 % based on the dry weight and the acrylamide polymer obtained in Preparation Example 3 was not added. Table 3 shows the result.

As shown in Tables 1 - 2, papers manufactured according to the conditions of the present invention exhibit rather a tendency of improved paper strength by the addition of anionic inorganic substances though addition of anionic inorganic substances usually changes the freeness.

It appears that when a proper amount of an anionic inorganic substance is present, the aggregation force of Hofmann PAM is lowered to an appropriate level so that the formation is controlled and the paper strength characteristics such as specific rupture strength, specific compression strength, internal bond strength and the like become excellent.

This effect is remarkable when the Hofmann decomposition reaction was carried out in a temperature range of 50 °C - 110 °C for a short time. The mechanism is not yet clarified, but it is clear that the paper strength effect of PAM obtained by the Hofmann decomposition reaction carried out at a high temperature for a short time can be enhanced by using an anionic inorganic substance.

Therefore, when it is contemplated that the formation is controlled and a paper of excellent strength is made even if the freeness is adversely affected to some extent, the present invention exhibits a great effect.

In addition, as shown in Table 3, papers made under the conditions within the scope of the present invention can exhibit excellent characteristics such as specific rupture strength, specific compression strength, internal bond strength and the like as compared with the case where an acrylamide polymer obtained in Preparation Example 3 or 4 is used alone while the papers made according to the present invention retains the same level of freeness as that in the case where the acrylamide polymer obtained in Preparation Example 4 is used alone.

TABLE - 1

	Hofmann decomposition conditions	Rate of addition		Freeness (ml)	Specific rupture strength	Specific compression strength	Internal bond strength (kg/cm)	
		(%/pipe)						
		Temperature (°C)	Time					Hofmann PAM
Example 1	80	15 sec	0.60	0.30	658	2.75	17.9	2.53
Example 2	80	15 sec	0.60	0.60	620	2.81	18.2	2.44
Example 3	80	15 sec	0.60	0.90	609	3.03	20.1	2.47
Example 4	80	15 sec	0.60	1.50	561	3.04	18.7	2.41
Comparison Example 1	20	2 hrs.	0.60	0.60	615	2.66	17.5	2.36
Comparison Example 2	20	2 hrs.	0.60	1.50	557	2.71	17.1	2.28

TABLE - 2

	Rate of addition (%/pipe)		Freeness (ml)	Specific rupture strength	Specific compression strength	Internal bond strength (kg/cm)
	Hofmann PAM	Colloidal silica				
Example 5	1.50	0.25	603	2.78	21.8	2.40
Example 6	1.50	0.50	606	2.83	21.7	2.51
Example 7	1.50	1.00	592	3.03	22.3	2.26
Comparison Example 3	1.50	-	550	2.48	20.1	2.09
Comparison Example 4	-	10.0	542	2.07	18.2	1.23

TABLE - 3

	Rate of Addition (%/pipe)		Freeness (ml)	Specific rupture strength	Specific compression strength	Internal bond strength (kg/cm)
	Copolymericization PAM	Hofmann PAM (C)				
Example 8	0.30	0.10	645	2.72	14.5	2.99
Example 9	0.20	0.20	645	2.70	14.4	3.07
Example 10	0.10	0.30	648	2.69	14.0	3.15
Comparison Example 5	0.40	-	469	2.47	12.6	1.92
Comparison Example 6	-	0.40	650	2.48	13.0	2.78

Industrial Applicability

The paper produced by the method of the present invention exhibits excellent specific rupture strength, specific compression strength, internal bond strength and the like.

Addition of the anionic inorganic substance is suitable for controlling the formation and producing a paper of high strength even if the freeness is somewhat adversely affected. When the cationic polyacrylamide is added, the level of freeness attained by using an acrylamide polymer alone can be retained, the formation is not lowered despite of good freeness which usually indicates lowering thereof, and the paper strength characteristic is excellent as compared with that when the acrylamide polymer is used alone.

Claims

1. A method for papermaking which comprises adding to a pulp slurry both an anionic inorganic substance and a cationic acrylamide polymer produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions at 50 - 110 °C for a short time, and then forming a wet pulp sheet followed by dehydration with a press and drying with a drier.
2. A method for papermaking which comprises adding to a pulp slurry both an anionic inorganic substance and a cationic acrylamide polymer (A) produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions of at least about pH 11 at a reaction temperature T (°C): 50 °C ≤ T ≤ 110 °C for a short reaction time t (sec) as shown in the following formulas,

$$t \text{ (sec)} \geq e^{\frac{15,150}{273+T}} \times 2.5 \times 10^{-20}$$

$$t \text{ (sec)} \leq e^{\frac{15,150}{273+T}} \times 10^{-18} + 30$$

and then forming a wet pulp sheet followed by dehydration with a press and drying with a dryer.

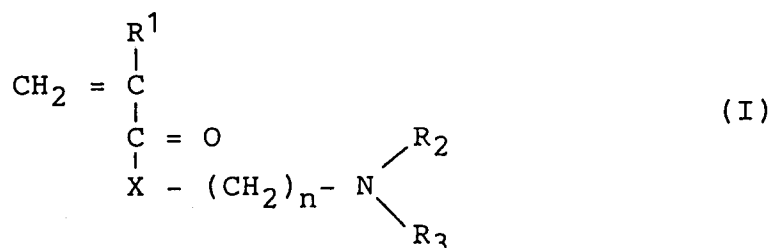
3. An additive for papermaking which comprises an anionic inorganic substance and a cationic acrylamide polymer produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions at 50 - 110 °C for a short time.
4. An additive for papermaking which comprises an anionic inorganic substance and a cationic acrylamide polymer (A) produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions of at least about pH 11 at a reaction temperature T (°C): 50 °C ≤ T ≤ 110 °C for a short reaction time t (sec) as shown in the following formulas,

$$t \text{ (sec)} \geq e^{\frac{15,150}{273+T}} \times 2.5 \times 10^{-20}$$

$$t \text{ (sec)} \leq e^{\frac{15,150}{273+T}} \times 10^{-18} + 30$$

5. A method for papermaking which comprises adding to a pulp slurry both a cationic acrylamide polymer

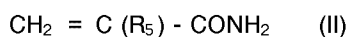
(A) produced by-reacting an acrylamide polymer with a hypohalogenite under alkaline conditions at 50 - 110° C for a short time and a cationic polyacrylamide (B) produced by copolymerizing
 (a) a cationic monomer of the general formula (I),



where R_1 is hydrogen or methyl, R_2 and R_3 are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, and n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary ammonium salts produced by the reaction of the compound of the general formula (I) with a quaternizing agent,

(b) an α,β -unsaturated carboxylic acid and/or salts thereof, and

(c) an acrylamide monomer of the general formula (II)



where R_5 is hydrogen or methyl, and then forming a wet pulp sheet followed by dehydration with a press and drying with a dryer.

6. A method for papermaking which comprises adding to a pulp slurry both a cationic acrylamide polymer (A) produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions of at least about pH 11 at a reaction temperature T (°C): $50^\circ\text{C} \leq T \leq 110^\circ\text{C}$ for a short reaction time t (sec) as shown in the following formulas,

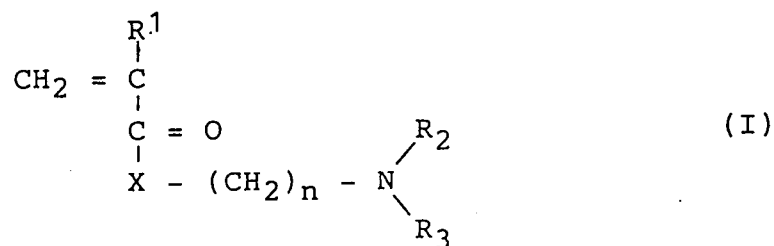
$$t \text{ (sec)} \geq e^{\frac{15,150}{273+T}} \times 2.5 \times 10^{-20}$$

$$t \text{ (sec)} \leq e^{\frac{15,150}{273+T}} \times 10^{-18} + 30$$

and

a cationic polyacrylamide (B) produced by copolymerizing

(a) a cationic monomer of the general formula (I),

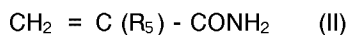


where R_1 is hydrogen or methyl, R_2 and R_3 are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, and n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary

ammonium salts produced by the reaction of the compound of the general formula (I) with a quaternizing agent,

(b) an α,β -unsaturated carboxylic acid and/or salts thereof, and

(c) an acrylamide monomer of the general formula (II)



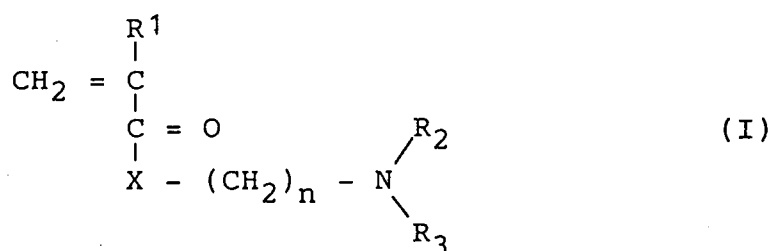
where R_5 is hydrogen or methyl,

and then forming a wet pulp sheet followed by dehydration with a press and drying with a dryer.

7. An additive for papermaking which comprises a cationic acrylamide polymer (A) produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions at 50 - 110°C for a short time and

a cationic polyacrylamide (B) produced by copolymerizing

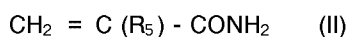
(a) a cationic monomer of the general formula (I),



where R_1 is hydrogen or methyl, R_2 and R_3 are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, and n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary ammonium salts produced by the reaction of the compound of the general formula (I) with a quaternizing agent,

(b) an α,β -unsaturated carboxylic acid and/or salts thereof, and

(c) an acrylamide monomer of the general formula (II)



where R_5 is hydrogen or methyl.

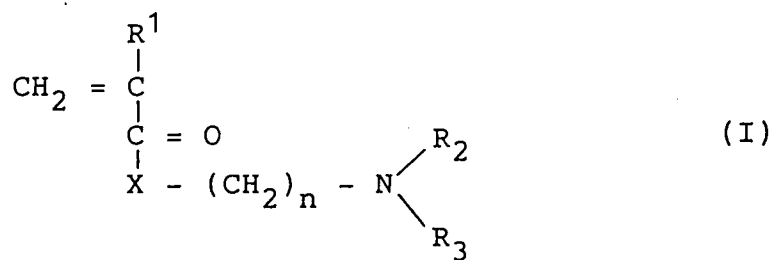
8. An additive for papermaking which comprises a cationic acrylamide polymer (A) produced by reacting an acrylamide polymer with a hypohalogenite under alkaline conditions of at least about pH 11 at a reaction temperature T (°C): $50^\circ\text{C} \leq T \leq 110^\circ\text{C}$ for a short reaction time t (sec) as shown in the following formulas,

$$t \text{ (sec)} \geq e^{\frac{15,150}{273+T}} \times 2.5 \times 10^{-20}$$

$$t \text{ (sec)} \leq e^{\frac{15,150}{273+T}} \times 10^{-18} + 30$$

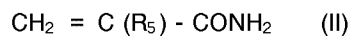
and a cationic polyacrylamide (B) produced by copolymerizing

(a) a cationic monomer of the general formula (I),



where R_1 is hydrogen or methyl, R_2 and R_3 are hydrogen or alkyl having 1 - 6 carbon atoms, X is O or NH, and n is an integer of 2 - 4, and/or organic or inorganic acid salts thereof, or quaternary ammonium salts produced by the reaction of the compound of the general formula (I) with a quaternizing agent,

(b) an α,β -unsaturated carboxylic acid and/or salts thereof, and
 (c) an acrylamide monomer of the general formula (II)



where R_5 is hydrogen or methyl.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00869

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ D21H17/45		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	D21H17/37-17/45	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	JP, A, 62-15391 (Seiko Kagaku Kogyo K.K.), January 23, 1987 (23. 01. 87), (Family: none)	1-4
A	JP, A, 60-65195 (Seiko Kagaku Kogyo K.K.), April 13, 1985 (13. 04. 85), (Family: none)	1-4
A	JP, B1, 46-27245 (Showa Kobunshi K.K.), September 27, 1966 (27. 09. 66), (Family: none)	1-4
A	JP, A, 58-108206 (Konan Kagaku Kogyo K.K.), June 28, 1983 (28. 06. 83), (Family: none)	1-4
A	JP, B1, 35-11302 (American Cyanamid Co.), August 16, 1960 (16. 08. 60), (Family: none)	1-4
¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search September 6, 1991 (06. 09. 91)		Date of Mailing of this International Search Report October 7, 1991 (07. 10. 91)
International Searching Authority Japanese Patent Office		Signature of Authorized Officer