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Description

This invention relates to a process for making paper. More particularly, it relates to a process for making paper which comprises forming a sheet from a pulp slurry containing a neutral sizing agent and optionally a filler using a specific cationic polymer as an agent for improving paper quality.

There has recently been employed a papermaking process such as so-called neutral or alkaline papermaking process which is carried out at pH 6 to 10, instead of an acidic papermaking process.

The neutral or alkaline papermaking process has advantages such as (1) a smaller energy for beating is used ; (2) corrosion of machine is less ; (3) the white water system can be closed ; (4) selection of fillers is not restricted and cheap calcium carbonate can be used ; (5) deterioration of paper with time is less ; and (6) printability of paper is good.

On the other hand, the neutral or alkaline papermaking process has drawbacks such as (1) expensive neutral sizing agents such as alkylketene dimers or alkenylsuccinic anhydrides, must be used instead of cheap rosin sizing agents, and further, such agents are poor in anchoring onto the pulp ; (2) fillers are poor in anchoring onto the pulp ; and (3) when the amount of calcium carbonate is increased, the strength of paper is lowered.

It is known to use Mannich reaction products of acrylamide polymer or acrylamide-acrylonitrile copolymer as an agent for reinforcing paper strength in the papermaking under neutral conditions, but these agents are insufficiently anchored onto the pulp, and hence, satisfactory reinforcing of paper strength is not expected. Besides, there are also known polymers prepared by converting a part or whole of the tertiary amines in the above Mannich reaction products into quaternary groups. Although the products can increase the paper strength reinforcing effect in the papermaking step under neutral conditions in comparison with non-quaternary products, the improvement is still insufficient, and the anchoring effect of the neutral sizing agent is poor and hence the desired sizing effect is not achieved. Moreover, there is known a copolymer comprising predominantly (meth)acrylamide and a quaternary product of dimethylaminoethyl(meth)acrylamide, but it is still poor in the paper strength reinforcing effect, and the sizing agent is poor in anchoring effect. There is also known a copolymer comprising predominantly (meth)acrylamide and a quaternary product of dimethylaminopropyl(meth)acrylamide, but it is still poor in the paper strength reinforcing effect like the above polymer, and the sizing agent is poor in anchoring effect and hence good sizing effect can not be achieved.

Besides, there is known a copolymer comprising predominantly (meth)acrylamide and diallyldimethylammonium chloride, but the sizing agent is poor in anchoring effect and hence the desired sizing effect can not be achieved, either.

Moreover, it is disclosed in JP-A-12521/1972 to use a polymer having a partial quaternary group which is produced by copolymerizing diallylamine and a copolymerizable vinyl monomer [e.g. (meth)acrylamide], followed by modifying with an agent for converting into quaternary group. However, such a polymer is particularly insufficient in anchoring of the sizing agent and hence can not give good sizing effect, while the paper strength reinforcing effect is improved.

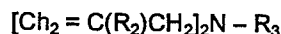
Although there are also known one or more of cationic polymer (e.g. polyamide/epichlorohydrin resin, etc.) and cationic starch, these are still not satisfactory in the effects. From these standpoints, it has been desired to develop an agent for improving paper quality which is excellent in the yield of the product per sizing agent and filler and has excellent paper strength reinforcing effect.

It is the object of the present invention to provide an improved process for making paper having sufficient sizing effect and excellent paper strength owing to the excellent yielding effect of each additive in the papermaking process particularly under neutral or alkaline condition, by using a neutral sizing agent and optionally a filler. This object could be achieved by the use of a specific agent for improving paper quality.

The present invention, therefore, provides a process for making paper which comprises forming a sheet from a pulp slurry at pH 6 to 10 in the presence of a neutral sizing agent and an agent for improving paper quality characterized in that the agent for improving paper quality is a cationic polymer which is prepared by copolymerizing (a) an acrylamide compound of the formula :



wherein R_1 is a hydrogen atom a methyl group, and (b) an inorganic or organic acid salt of a diallylamine compound of the formula :



wherein R_2 is a hydrogen atom or a methyl group, R_3 is a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

The agent for improving paper quality which is used may be one which has been prepared by copolymerization in the presence of (c) a vinyl monomer copolymerizable with said acrylamide compound and/or said diallylamine compound salt.

The acrylamide compound used as the component (a) in this invention is acrylamide or methacrylamide.

5 The diallylamines as the component (b) include, for example, diallylamine, diallylmethylamine, diallylethylamine and diallylbutylamine, and these are used in the form of a salt with an inorganic acid (e.g. hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid) and an organic acid (e.g. formic acid, acetic acid and propionic acid). Among these, the diallylamine salts are most preferable.

10 The component (c) which is optionally used in this invention includes any nonionic, cationic or anionic vinyl monomers which are copolymerizable with the component (a) and/or the component (b). Examples of the nonionic monomer are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, acrylonitrile, methacrylonitrile, styrene, hydroxyethyl acrylate, hydroxyethyl methacrylate and vinyl acetate.

15 Examples of the cationic monomer are dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminopropylacrylamide and dimethylaminopropylmethacrylamide or the quaternary derivatives of these compounds, diallyldimethylammonium chloride, vinylpyridine and vinylpyrrolidone, and the like.

Examples of the anionic monomer are acrylic acid, methacrylic acid, vinylsulfonic acid and maleic acid.

20 The ratio of the components (a), (b) and (c) used in the copolymerization of this invention is preferably the component (a) : 40 to 99% by mole, more preferably 50 to 97% by mole, the component (b) : 1 to 60% by mole, more preferably 3 to 50% by mole, and the component (c) can be used in any amount unless the effect of this invention is inhibited but may be restricted by the water solubility and ionic properties thereof. In case of a nonionic monomer, it should be used within such an amount that the produced polymer does not lose its water solubility. In case of a cationic monomer, it is used in an amount of not more than 40% by mole, preferably not more than 30% by mole. Besides, in case of an anionic monomer, it is used in the range of less than the amount
25 of the component (b).

When the component (a) is used in an amount of less than 40% by mole or the component (b) is used in an amount of less than 1% by mole, the effect of this invention can not sufficiently be achieved, and when the component (c) is used in an amount of over 40% by mole, it is the same.

30 The production of the copolymer in this invention can be carried out by a known process, and the polymerization manner is not specified, but it is preferably done by reacting in water or a mixed solvent of water and a water soluble solvent in the presence of a polymerization initiator.

35 The polymerization initiator includes any conventional initiators, for example, persulfates (e.g. ammonium persulfate and potassium persulfate, azo compounds (e.g. 2,2'-diamidinyl-2,2'-azopropane dihydrochloride and azobisisobutyronitrile) and peroxides (e.g. di-t-butyl peroxide, cumene hydroperoxide and hydrogen peroxide). There may also be used known redox initiators, such as potassium persulfate and sodium bisulfide, or a combination with tertiary amines.

The polymerization is usually carried out at 10 to 100°C, preferably at 40 to 80°C, for 1 to 10 hours. The polymerization may be done in the presence of oxygen, but preferably done under an atmosphere of an inert gas such as nitrogen.

40 The component (a), component (b) and optionally component (c) may wholly be charged at one time and then subjected to the polymerization, or alternatively, a part or the whole of a certain component may be charged after initiation of the polymerization of other components, and the component may be added continuously or partially.

45 In this invention, the cationic polymer thus prepared is used as a paper quality improver, and the amount thereof depends on factors like the kind of paper, desired degree of sizing and the desired strength of paper. Usually it is used in an amount of 0.01 to 2% by weight, preferably 0.05 to 1% by weight, when calculated as solid polymer based on the weight of the paper in dry state.

The cationic polymer used in this invention may be used alone or in combination with other ingredients (e.g. sizing anchoring agent and yield improver).

50 The Filler used optionally in this invention includes, for example, calcium carbonate, kaolin, clay, talc, TiO₂ and satin white. The neutral sizing agent used in this invention includes, for example, alkylketene dimers, alkenylsuccinic anhydride, isocyanate aziridine derivatives, carbonyl derivatives and fatty acid anhydrides.

55 According to this invention, the sheet forming is carried out by using the above cationic polymer, a neutral sizing agent and optionally a filler at pH 6 to 10. The process is not specified but includes any conventional processes. In the so-called beater-addition process, a filler and a sizing agent are both added to an aqueous suspension of pulp fibers and the mixture is subjected to the sheet forming. In the beater-addition process, the order of addition of additives is not specified.

The cationic polymer of this invention may be used alone or in combination with other ingredients (e.g. siz-

ing anchoring agent and yield improvers).

This invention is illustrated by the following examples, but is not limited thereto. In the examples, "%" means % by weight unless specified otherwise.

5 Preparation 1

A 50% aqueous solution of diallylamine hydrochloride (42.8 g, 0.16 mole), a 50% aqueous solution of acrylamide (34.1 g, 0.24 mole), isopropyl alcohol (7.7 g) and deionized water (171.6 g) were charged into a reactor provided with a stirrer, and the mixture was regulated to pH 7.0 with a slight amount of 28% aqueous sodium hydroxide. The reactor was purged with nitrogen gas to remove oxygen within the vessel, and thereafter, ammonium persulfate (0.12 g) was added at 55°C, and the mixture was reacted at 55°C for 6 hours. By quantitative determination of the unreacted monomer, it was confirmed that the degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 4.3, and a Brookfield viscosity (25°C) of 6.5 Pa.s (65 ps).

15 Preparation 2

A 50% aqueous solution of diallylamine hydrochloride (10.7 g, 0.04 mole) and deionized water (144.1 g) were charged into a reactor provided with a stirrer, and the mixture was regulated to pH 7.0 with a slight amount of 28% aqueous sodium hydroxide. The reactor was purged with nitrogen gas to remove oxygen within the vessel, and thereafter, ammonium persulfate (0.28 g) was added thereto at 70°C. With keeping the inner temperature at 70°C, a 50% acrylamide solution (51.2 g, 0.36 mole) was added to the reaction system over a period of 2 hours. Thereafter, the mixture was reacted at 70°C for 2 hours. By quantitative determination of the unreacted monomer, it was confirmed that the degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 3.5, and a Brookfield viscosity (25°C) of 5 Pa.s (50 ps).

25 Preparation 3

A 98% diallylmethylamine hydrochloride (3.8 g, 0.025 mole) solution and deionized water (97.6 g) were charged into a reactor provided with a stirrer, and the mixture was regulated to pH 7.0. The reactor was purged with nitrogen gas to remove oxygen within the vessel, and thereafter, ammonium persulfate (0.1 g) was added thereto at 70°C. With keeping the inner temperature at 70°C, a 50% aqueous solution of acrylamide (32.0 g, 0.225 mole) was added to the reaction system over a period of 2 hours. Thereafter, the mixture was reacted at 70°C for 2 hours. By quantitative determination of the unreacted monomer, it was confirmed that the degree of reaction was 99% or more.

35 The product had a polymer content of 15%, pH 3.9, and a Brookfield viscosity (25°C) of 5.5 Pa.s (55 ps).

Preparation 4

A 50% aqueous solution of diallylamine hydrochloride (10.7 g, 0.04 mole) and deionized water (141.8 g) were charged into a reactor provided with a stirrer, and the mixture was regulated to pH 6.8 with a slight amount of 28% aqueous sodium hydroxide. The reactor was purged with nitrogen gas to remove oxygen within the vessel, and thereafter, 2,2'-diamidiny-2,2'-azopropane dihydrochloride (0.27 g) was added thereto at 70°C. With keeping the inner temperature at 70°C, a mixture of a 50% aqueous solution of acrylamide (40.9 g, 0.288 mole) and acrylonitrile (3.8 g, 0.072 mole) was added to the reaction system over a period of 3 hours. Thereafter, the mixture was reacted at 70°C for 3 hours. By quantitative determination of unreacted monomer, it was confirmed that the degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 3.4, and a Brookfield viscosity (25°C) of 4.3 Pa.s (43 ps).

Preparations 5 to 12

50 In the same manner as described in Preparations 1 to 4 except that the monomer and monomer composition were changed, there were produced various polymers. The results are shown in Table 1.

Table 1

Prep. No.	Monomer (a) (% by mole)	Monomer (b) (% by mole)	Monomer (c) (% by mole)	Concentration of aqueous polymer solution	Viscosity of aqueous polymer solution (25°C)	pH of aqueous polymer solution
5	Acrylamide (70)	Diallylamine sulfate (30)	-	15 %	5.5 Pa.s (55 ps)	3.9
6	Acrylamide (45)	Diallylamine acetate (25)	Acrylonitrile (30)	15 %	4.8 Pa.s (48 ps)	4.2
7	Acrylamide (65)	Diallylamine hydrochloride (15)	Vinyl acetate (20)	15 %	3.7 Pa.s (39 ps)	4.2
8	Acrylamide (70)	Diallylamine hydrochloride (20)	Acrylic acid (10)	15 %	4.5 Pa.s (45 ps)	3.8
9	Acrylamide (80)	Diallylamine hydrochloride (10)	Dimethylaminoethyl acrylate (10)	15 %	3.8 Pa.s (38 ps)	4.0

Prep. No.	Monomer (a) (% by mole)	Monomer (b) (% by mole)	Monomer (c) (% by mole)	Concentration of aqueous polymer solution	Viscosity of aqueous polymer solution (25°C)	pH of aqueous polymer solu- tion
10	Acrylamide (40)	Diallylamine hydrochloride (60)	-	15 %	5.4 Pa.s (54 ps)	3.8
11	Methacryl- amide (45)	Diallyl- methylamine sulfate (10)	-	15 %	7.3 Pa.s (73 ps)	3.9
12	Acrylamide (80)	Dimethallyl- amine hydro- chloride (20)	-	15 %	6.5 Pa.s (65 ps)	4.1

Reference Preparation 1

A 15% aqueous solution of acrylamide was reacted with ammonium persulfate (0.5% by weight per weight of acrylamide), where the degree of polymerization was controlled by using isopropyl alcohol to give an aqueous solution of polyacrylamide having pH 3.4 and a viscosity of 11.4 Pa.s (114 ps).

Thereafter, to the aqueous solution of polyacrylamide (473.8 g, 1.0 mole calculated as the acid amide group) were added a 50% aqueous solution of dimethylamine (19.8 g, 0.22 mole) and a 37% formalin solution (16.2 g, 0.2 mole), and the mixture was subjected to Mannich reaction by keeping it at 45°C for one hour. To the aqueous solution was further added dimethyl sulfate (22.7 g, 0.18 mole), and the mixture was kept at 15-20°C for about 5 hours, by which the reaction for conversion of the amino groups into quaternary ammonium group was completed. After completion of the conversion reaction the aqueous solution of polymer was regulated to the desired pH and concentration with aqueous sodium carbonate solution and deionized water to give an aqueous solution of polymer having a polymer content of 15%, pH 3.2 and a Brookfield viscosity (25°C) of 2.5 Pa.s (25 ps).

Reference Preparation 2

A 50% aqueous solution of acrylamide (48.3 g, 0.34 mole), dimethylaminoethyl methacrylate which was converted into a quaternary ammonium compound with methyl chloride (12.5 g, 0.06 mole), deionized water (176.0 g), and isopropyl alcohol (7.3 g) were charged into a reactor provided with a stirrer, and the reactor was purged well with nitrogen gas. Ammonium persulfate (0.21 g) was added thereto at 60°C, and thereafter, the mixture was reacted at 60°C for 4 hours. It was confirmed that the degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 3.2, and a Brookfield viscosity (25°C) of 3.7 Pa.s (37 ps).

Reference Preparation 3

A 50% aqueous solution of acrylamide (51.2 g, 0.36 mole), dimethylaminopropyl methacrylate which was converted into a quaternary ammonium compound with methyl chloride (8.83 g, 0.04 mole), deionized water (162.6 g), and isopropyl alcohol (6.9 g) were charged into a reactor provided with a stirrer, and the reactor was purged well with nitrogen gas. Ammonium persulfate (0.19 g) was added thereto at 60°C, and thereafter, the mixture was reacted at 60°C for 4 hours. The degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 4.7, and a Brookfield viscosity (25°C) of 4.2 Pa.s (42 ps).

Reference Preparation 4

A 70% diallyldimethylammonium chloride (5.8 g, 0.025 mole) and deionized water (95.7 g) were charged into a reactor provided with a stirrer, and the mixture was regulated to pH 7.0 with a slight amount of a 28% aqueous sodium hydroxide solution. Thereafter, the reactor was purged with nitrogen gas to remove oxygen within the vessel, and then ammonium persulfate (0.10 g) was added thereto at 70°C. Thereafter, keeping the inner temperature at 70°C, a 50% acrylamide solution (32.0 g, 0.225 mole) was added over a period of 2 hours. Thereafter, the mixture was reacted at 70°C for 2 hours. By quantitative determination of the unreacted monomer, it was confirmed that the degree of reaction was 99% or more.

The product had a polymer content of 15%, pH 3.9, and a Brookfield viscosity (25°C) of 4.6 Pa.s (46 ps).

Examples 1 to 12 and Reference Examples 1 to 4

The sheet forming was carried out by using the cationic polymers as prepared in Preparations and Reference Preparations as an agent for neutral papermaking.

By using N/L (1/1) BKP (C.S.F = 410 ml), to a slurry of pulp (pulp concentration : 7.5 g/l) were added CaCO₃ (10% per pulp weight), AQUAPEL 12 (an alkylketene dimer type neutral sizing agent, manufactured by DIC Hercules, 0.1% per pulp weight) and the cationic polymer (0.15% per pulp weight), and the mixture was subjected to sheet forming at a slurry pH of 8.5 so that the basis weight became 60 g/m² (based on the regulation by TAPPI). Thereafter, the paper was dehydrated at 4 kg/cm² for 7 minutes and dried at 110°C for 4 minutes. Thereafter, the sheet was kept at 20°C, 65 RH for 15 hours in order to control the humidity, and then the various properties of the paper was measured. The results are shown in Table 2. The properties were measured in the following manner.

Internal bond was measured with the Internal Bond Tester (manufactured by Kumagaya Riki Kogyo K.K.). Stöckigt sizing degree was measured in a similar manner as described in JIS-P-8122 (a test method for measur-

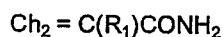
ing Stöckigt sizing degree of paper). The yield per CaCO_3 was measured in a similar manner as described in JIS-P-8128 (a test method for measuring the ash content of paper and paper board).

Table 2

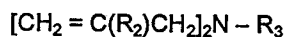
Sample No.	Internal bond (kg/cm)	Stöckigt sizing degree (second)	Yield per CaCO_3 (%)
Ex. 1	2.69	29.8	76.8
" 2	2.74	30.2	77.3
" 3	2.39	21.3	67.5
" 4	2.68	29.4	73.4
" 5	2.60	28.1	75.3
" 6	2.73	28.5	74.7
" 7	2.72	29.0	72.8
" 8	2.80	29.7	73.1
" 9	2.61	29.9	74.2
" 10	2.75	28.6	75.6
" 11	2.48	20.7	68.7
" 12	2.76	29.5	74.7
Ref. Ex. 1	2.50	7.5	59.6
" 2	1.98	6.8	51.2
" 3	1.97	9.4	60.3
" 4	2.10	8.5	52.5
Control	1.68	0	14.4

Claims

1. A process for making paper which comprises forming a sheet from a pulp slurry at pH 6 to 10 in the presence of a neutral sizing agent and an agent for improving paper quality characterized in that the agent for improving paper quality is cationic polymer which is prepared by copolymerizing an acrylamide compound of the formula :



wherein R_1 is a hydrogen atom or a methyl group, and an inorganic or organic acid salt or a diallylamine compound of the formula :



wherein R_2 is a hydrogen atom or a methyl group, R_3 is a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

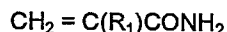
2. The process according to claim 1, wherein a filler is used for forming the sheet from the pulp slurry.

3. The process according to claim 1 or 2, wherein the agent for improving paper quality used has been

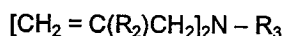
prepared by copolymerization in the presence of a vinyl monomer copolymerizable with said acrylamide compound and/or said diallylamine compound salt.

5 Ansprüche

1. Verfahren zur Herstellung von Papier, das das Erzeugen eines Blattes aus einer Pulpenaufschlammung bei einem pH-Wert von 6 bis 10 in Gegenwart eines neutralen Leimungsmittels und eines Mittels zur Verbesserung der Papierqualität umfaßt, dadurch gekennzeichnet, daß das Mittel zur Verbesserung der Papierqualität ein kationisches Polymer ist, das durch die Copolymerisation einer Acrylamidverbindung der Formel



- in der R_1 ein Wasserstoffatom oder eine Methylgruppe ist, und eines anorganischen oder organischen Salzes einer Diallylaminverbindung der Formel



- hergestellt worden ist, in der R_2 ein Wasserstoffatom oder eine Methylgruppe und R_3 ein Wasserstoffatom oder ein Alkylrest mit 1 bis 6 Kohlenstoffatomen ist.

2. Verfahren nach Anspruch 1, in dem ein Füllmittel zur Erzeugung des Blattes aus der Pulpenaufschlammung verwendet wird.

3. Verfahren nach Anspruch 1 oder 2, in dem das Mittel zur Verbesserung der Papierqualität durch Copolymerisation in Gegenwart eines Vinylmonomers hergestellt worden ist, das mit der Acrylamidverbindung und/oder dem Salz der Diallylaminverbindung copolymerisierbar ist.

Revendications

1. Un procédé de fabrication du papier qui comprend la formation d'une feuille à partir d'une bouillie de pâte à pH 6 à 10 en présence d'un agent d'encollage neutre et d'un agent pour améliorer la qualité du papier, caractérisé en ce que l'agent pour améliorer la qualité du papier est un polymère cationique qui est préparé par copolymérisation d'un composé acrylamide de formule :



dans laquelle R_1 est un atome d'hydrogène ou un groupe méthyle, et un sel d'acide organique ou inorganique d'un composé diallylamine de formule :



dans laquelle R_2 est un atome d'hydrogène ou un groupe méthyle, R_3 est un atome d'hydrogène ou un groupe alkyle ayant 1 à 6 atomes de carbone.

2. Le procédé selon la revendication 1, selon lequel une charge est utilisée pour former la feuille à partir de la bouillie de pâte.

3. Le procédé selon la revendication 1 ou 2, selon lequel l'agent pour améliorer la qualité du papier utilisé a été préparé par copolymérisation en présence d'un monomère vinylique copolymérisable avec ledit composé acrylamide et/ou ledit sel du composé diallylamine.