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(54) **SURFACE PAPER STRENGTH ENHANCER, COATING LIQUID, AND METHOD FOR PRODUCING PAPER**

(57) The present invention relates to: a surface paper strength enhancer containing a polymer (A) comprising, as reactive components, a (meth)acrylamide (a1), a (meth)acrylamide (a2) having a carboxy group, an ethylenically unsaturated monomer (a3) having a sulfo group, and a crosslinkable monomer (a4), wherein a solution of the surface paper strength enhancer

having a non-volatile concentration of 20 wt% has a viscosity of 100-5,000 mPa·s at a temperature of 25°C; a coating liquid containing the surface paper strength enhancer; and a method for producing paper, the method comprising a step for applying the coating liquid to the surface of a base paper and then drying the coating liquid.

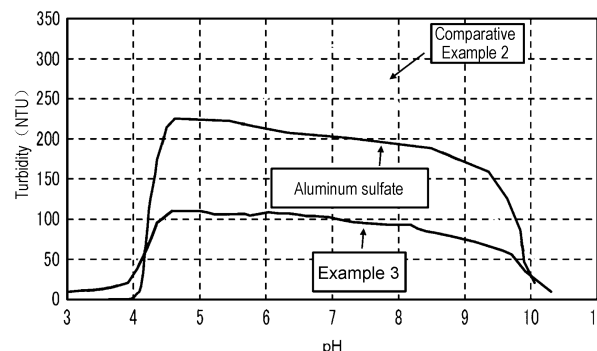


FIG. 1

Description

Technical Field

- 5 **[0001]** The present invention relates to a surface paper strength enhancer, a coating liquid, and a method for producing paper.

Related Art

- 10 **[0002]** In recent years, due to growing environmental awareness and demands for cost reduction, the proportion of recycled paper pulp has been increasing and the weight of base paper itself has been decreasing. For this reason, it has become difficult to maintain paper strength by internally adding a paper strength enhancer to raw material pulp alone, due to the influence of contaminants such as fine fibers and calcium ions contained in the paper. To compensate for this strength, surface paper strength enhancers such as starch and polyacrylamide are applied to the surface
15 of base paper. Moreover, in surface coating, the speed of papermaking machines has been increasing to improve productivity, and film transfer type size presses such as gate rolls and rod metering have been applied in place of the conventional two-roll size press method, and there is a demand for penetrability of coating liquid and a high paper strength enhancing effect.

- [0003]** To achieve a high paper strength enhancing effect, one approach is, for example, to enhance the molecular weight of polyacrylamide, which is a paper strength enhancer. However, in that case, the surface paper strength enhancer becomes less likely to penetrate into the interior of the paper, and the paper strength enhancing effect also becomes insufficient. Therefore, as an alternative approach, attention is also paid to the composition of the surface paper strength enhancer, and it is possible to cause it to interact with an aluminum compound contained in base paper without impairing penetrability.

- 25 **[0004]** As such a technique, for example, a surface paper strength enhancer (Patent Document 1) including a polymer of a monomer component containing (meth)acrylamide, N-substituted (meth)acrylamides, an unsaturated monomer having a sulfonic acid group, and an α,β -unsaturated dicarboxylic acid is known. In this technique, by causing interaction between an aluminum compound contained in base paper and the surface paper strength enhancer, a pseudo polyion complex (PIC) is formed, the surface paper strength enhancer is fixed to the paper, and a high
30 paper strength enhancing effect is imparted. However, the effect was still insufficient.

Citation List

Patent Documents

- 35 **[0005]** Patent Document 1: Japanese Patent Laid-Open No. 2019-173257

SUMMARY

40 Technical Problem

- [0006]** An object of the present invention is to provide a surface paper strength enhancer that excels in paper strength enhancing effect.

45 Solution to Problem

- [0007]** The inventors of the present invention focused on the composition of monomer components and the physical properties of the polymer, and through extensive studies, found a solution to the aforementioned problem, and completed the present invention. Specifically, the present invention relates to the following surface paper strength enhancer, coating liquid, and method for producing paper.
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1. A surface paper strength enhancer containing a polymer (A) comprising, as reactive components, a (meth)acrylamide (a1), a (meth)acrylamide (a2) having a carboxy group, an ethylenically unsaturated monomer (a3) having a sulfo group, and a crosslinkable monomer (a4), in which
55 a solution of the surface paper strength enhancer having a non-volatile content concentration of 20% by weight has a viscosity of 100 to 5,000 mPa·s at a temperature of 25°C.
2. The surface paper strength enhancer according to item 1, in which the reactive components further contain an ethylenically unsaturated monomer (a5) having a carboxy group other than the component (a2).

3. The surface paper strength enhancer according to item 1, in which, with total reactive components being 100 mol%, the component (a1) is 72 to 97 mol%, the component (a2) is 0.01 to 15 mol%, the component (a3) is 0.4 to 10 mol%, and the component (a4) is 0.001 to 8 mol%.

4. The surface paper strength enhancer according to item 1, in which, in an aqueous solution containing the surface paper strength enhancer at 1% by weight and aluminum sulfate at 0.5% by weight in terms of non-volatile content concentration, when a maximum turbidity value at pH 5 to 8 is X and a minimum turbidity value is Y in units of NTU, $10 \leq X \leq 200$ and $X - Y \leq 50$ are satisfied.

5. A coating liquid containing the surface paper strength enhancer according to any one of items 1 to 4.

6. A method for producing paper, including a step of applying the coating liquid according to item 5 to a surface of a base paper and drying the base paper.

7. The method for producing paper according to item 6, in which the base paper includes an aluminum compound.

Effects of Invention

[0008] According to the paper strength enhancer of the present invention, an excellent paper strength enhancing effect is exhibited when made into paper.

BRIEF DESCRIPTION OF DRAWINGS

[0009] [FIG. 1] is a graph of turbidity of an aluminum sulfate aqueous solution, and mixed liquids of the surface paper strength enhancer of Example 3 and Comparative Example 2 with aluminum sulfate.

DESCRIPTION OF THE EMBODIMENTS

[0010] The paper strength enhancer of the present invention includes a polymer (A) including (meth)acrylamide (a1) (hereinafter referred to as component (a1)), a (meth)acrylamide (a2) having a carboxy group (hereinafter referred to as component (a2)), an ethylenically unsaturated monomer (a3) having a sulfo group (hereinafter referred to as component (a3)), and a crosslinkable monomer (a4) (hereinafter referred to as component (a4)) as reactive components (hereinafter referred to as polymer (A)). Hereinafter, (meth)acryl refers to methacryl and/or acryl, (meth)acrylate refers to methacrylate and/or acrylate, and ethylenically unsaturated refers to having one or more carbon-carbon double bonds and/or carbon-carbon triple bonds in a molecule (the same applies hereinafter).

[0011] The component (a1) is methacrylamide or acrylamide. These may be used alone or two or more thereof may be used in combination.

[0012] The molar ratio of the component (a1) is preferably 72 to 97 mol%, more preferably 75 to 97 mol%, and further preferably 80 to 95 mol%, based on 100 mol% of the total reactive components.

[0013] The component (a2) is a (meth)acrylamide having a carboxy group. A carboxy group is a group represented by -COOH. By using the component (a2), the surface paper strength enhancer is more likely to interact with the aluminum compound included in the base paper, and as a result, a high paper strength enhancing effect is more likely to be exhibited.

[0014] Examples of the component (a2) include (meth)acrylamide alkanolic acids such as N-(meth)acryloylglycine (2-((meth)acryloylamino)acetic acid), 3-(meth)acrylamidopropionic acid, 4-(meth)acrylamidebutanoic acid, 5-(meth)acrylamidopentanoic acid, and 6-(meth)acrylamidohexanoic acid;

(meth)acrylamide alkyl monoalkanoic acids such as 3-(meth)acrylamido-2-methylbutanoic acid, 3-(meth)acrylamido-3-methylbutanoic acid, and 4-(meth)acrylamido-3,3-dimethylhexanoic acid; and

2-(meth)acrylamido-N-glycolic acid, and the like. These may be used alone or in a combination of two or more.

Among these, 2-(meth)acrylamido-N-glycolic acid is preferred in that it has a hydroxy group in addition to a carboxy group that is more likely to interact with the aluminum compound included in the base paper.

[0015] The component (a2) may be used as-is after being prepared by adding one or more selected from monoalkanoic acids, alkyl monoalkanoic acids, alkanedicarboxylic acids, hydroxycarboxylic acids, aldehyde alkanolic acids, and salts thereof to the reactive components, and reacting with the component (a1).

[0016] Examples of monoalkanoic acids include monoalkanoic acids such as acetic acid, propionic acid, butanoic acid, pentanoic acid, and hexanoic acid.

[0017] Examples of alkyl monoalkanoic acids include 2-methylbutanoic acid, 3-methylbutanoic acid, and 3,3-dimethylhexanoic acid.

[0018] Examples of alkanedicarboxylic acids include succinic acid and oxalic acid.

[0019] Examples of hydroxycarboxylic acids include citric acid and glycolic acid.

[0020] Examples of aldehyde carboxylic acids include glyoxylic acid.

[0021] Examples of salts thereof include alkali metal salts such as lithium, sodium, and potassium salts of the monoalkanoic acids, alkyl monoalkanoic acids, alkanedicarboxylic acids, hydroxycarboxylic acids, or aldehyde alkanic acids; alkaline earth metal salts such as magnesium salts and calcium salts; ammonium salts such as ammonia; and organic amine salts such as trimethylamine, triethylamine, trimethanolamine, and triethanolamine. These may be used alone or two or more thereof may be used in combination.

[0022] The molar ratio of the component (a2) is preferably 0.01 to 15 mol%, more preferably 0.05 to 12 mol%, and further preferably 0.1 to 10 mol%, based on 100 mol% of the total reactive components, from the standpoint that the surface paper strength enhancer is more likely to interact with the aluminum compound contained in the base paper and exhibit a high paper strength enhancing effect, and additionally, the cost of the surface paper strength enhancer is reduced.

[0023] The component (a3) is an ethylenically unsaturated monomer having a sulfo group. A sulfo group is a group represented by $-SO_3H$. The use of the component (a3) provides a surface paper strength enhancer having a prescribed viscosity, which facilitates penetration into the interior of the base paper upon coating, and also tends to exhibit a high paper strength enhancing effect.

[0024] Examples of component (a3) include vinylsulfonic acid, methallylsulfonic acid, and p-styrenesulfonic acid. Here, these components (a3) may be used as salts such as alkali metal salts such as sodium and potassium, or ammonium salts. These may be used alone or two or more thereof may be used in combination. Among these, methallylsulfonic acid or a salt thereof is preferable, and sodium methallylsulfonate is more preferable.

[0025] The molar ratio of the component (a3) is preferably 0.4 to 10 mol%, more preferably 0.6 to 8 mol%, and further preferably 0.8 to 5 mol%, based on 100 mol% of the total reactive components, from the standpoint of obtaining a surface paper strength enhancer having a prescribed viscosity and facilitating the exhibition of a high paper strength enhancing effect.

[0026] The component (a4) is a crosslinkable monomer.

[0027] Examples of component (a4) include N-alkyl(meth)acrylamides such as N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, and N-isopropyl(meth)acrylamide, N-t-butyl(meth)acrylamide;

N,N-dialkyl(meth)acrylamides such as N,N-dimethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, and N,N-diisopropyl(meth)acrylamide;

N,N'-alkylenebis(meth)acrylamides such as N,N'-methylenebis(meth)acrylamide, and N,N'-ethylenebis(meth)acrylamide;

crosslinkable monomers having a triallyl group such as triallyl isocyanurate, triallyl trimellitate, triallylamine, and triallyl(meth)acrylamide; and

triazines having a (meth)acryloyl group such as 1,3,5-triacryloyl-1,3,5-triazine, and 1,3,5-triacryloylhexahydro-1,3,5-triazine. These may be used alone or two or more thereof may be used in combination.

[0028] Among these, N,N-dialkyl(meth)acrylamides and N,N'-alkylenebis(meth)acrylamides are preferable, and N,N-dimethyl(meth)acrylamide and N,N'-methylenebis(meth)acrylamide are more preferable.

[0029] The molar ratio of the component (a4) is preferably 0.001 to 8 mol%, more preferably 0.003 to 7 mol%, and further preferably 0.005 to 5.5 mol%, based on 100 mol% of the total reactive components, from the viewpoint of suppressing excessive crosslinking reactions and facilitating reduction in the occurrence of gelation.

[0030] The reactive component may further include an ethylenically unsaturated monomer having a carboxy group other than the component (a2) (hereinafter referred to as component (a5)).

[0031] Examples of component (a5) include ethylenically unsaturated monocarboxylic acids such as (meth)acrylic acid, 3-butenic acid, 4-pentenoic acid, 5-hexenoic acid, and 4-methylhexene;

ethylenically unsaturated dicarboxylic acids such as itaconic acid, fumaric acid, maleic acid, citraconic acid, and muconic acid;

ethylenically unsaturated monocarboxylic acid anhydrides such as (meth) acrylic acid anhydride; and

ethylenically unsaturated dicarboxylic acid anhydrides such as itaconic acid anhydride, maleic acid anhydride, and citraconic acid anhydride, and the like. These components (a5) may be used as salts such as alkali metal salts of lithium, sodium, potassium, and the like; alkaline earth metal salts such as magnesium salts and calcium salts; ammonium salts such as ammonia; organic amine salts such as trimethylamine, triethylamine, trimethanolamine, and triethanolamine. These may be used alone or two or more thereof may be used in combination. Among these, (meth)acrylic acid, (meth) acrylic acid anhydride, itaconic acid, and itaconic acid anhydride are preferable.

[0032] The molar ratio of the component (a5) is preferably 10 mol% or less, more preferably 5 mol% or less, and further preferably 3 mol% or less, based on 100 mol% of the total reactive components, from the viewpoint of securing

a sufficient paper strength enhancing effect of the surface paper strength enhancer.

[0033] The reactive component may further include monomers (a6) other than the components (a1) to (a5) (hereinafter referred to as component (a6)).

[0034] Examples of component (a6) include ethylenically unsaturated monomers having a secondary amino group such as diallylamine;

ethylenically unsaturated monomers having a tertiary amino group such as (meth)acrylates having a tertiary amino group such as N,N-dimethylaminoethyl (meth)acrylate and N,N-diethylaminoethyl (meth)acrylate, and (meth)acrylamides having a tertiary amino group such as N,N-dimethylaminopropyl (meth)acrylamide and N,N-diethylaminopropyl (meth)acrylamide;

quaternary salts obtained by reacting a polymerizable monomer having a secondary amino group or a polymerizable monomer having a tertiary amino group with a quaternizing agent (examples of the quaternary salts include inorganic acid salts such as hydrochloride and sulfate salts; organic acid salts such as acetate salts, and the like; examples of the quaternizing agent include methyl chloride, benzyl chloride, dimethyl sulfate, epichlorohydrin, and the like);

monomers having an aromatic ring such as styrene, α -methylstyrene, and vinyl toluene;

alkyl(meth)acrylates such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, n-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, and cyclohexyl(meth)acrylate;

vinyl carboxylates such as vinyl acetate and vinyl propionate;

nitriles such as acrylonitrile;

mercaptans such as 2-mercaptoethanol and n-dodecyl mercaptan;

alcohols such as ethanol, isopropyl alcohol, and n-pentyl alcohol;

aromatic compounds such as α -methylstyrene dimer, ethylbenzene, isopropylbenzene, and cumene; and

carbon tetrachloride. These may be used alone or two or more thereof may be used in combination.

[0035] The molar ratio of the component (a6), with the total reactive components taken as 100 mol%, is preferably 10 mol% or less, more preferably 5 mol% or less, and further preferably 3 mol% or less.

[0036] In manufacture of (meth)acrylamide polymers, inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid; inorganic acid salts such as sodium sulfate, potassium sulfate, and ammonium sulfate; inorganic bases such as sodium hydroxide, potassium hydroxide, and calcium hydroxide; starches such as oxidized starch, phosphate esterified starch, urea phosphate esterified starch, etherified starch, crosslinked starch, APS modified starch, enzyme modified starch, cationized starch, and amphoteric starch; and agents such as polyvinyl alcohol, urea, an antifoaming agent, an antioxidant, a preservative, and an antimicrobial agent may be added may be added. These may be used alone or two or more thereof may be used in combination.

[0037] The polymer (A) of the present invention may be produced by, for example, a method in which a solution of a polymerization initiator is added to a solution containing the components (a1) to (a4), and optionally components (a5) to (a6) and additives, in a solvent prepared in advance in a reaction device, followed by a reaction. The polymerization initiator and the solvent may also be added as appropriate during or after the reaction.

[0038] Examples of solvents include water and an organic solvent, and these may be used alone or two or more thereof may be used in combination.

[0039] Examples of water include tap water, ultrapure water, pure water, deionized water, hard water, soft water, and industrial water. These may be used alone or two or more thereof may be used in combination.

[0040] Examples of organic solvents include alcohols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, n-hexyl alcohol, n-octyl alcohol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, and diacetone alcohol; and ethers such as ethylene glycol monobutyl ether, propylene glycol monomethyl ether, and propylene glycol monoethyl ether. These may be used alone or two or more thereof may be used in combination.

[0041] Among these, water is preferable from the standpoint of sufficiently dissolving and dispersing the components (a1) to (a6).

[0042] The amount of the solvent used may be adjusted so that the non-volatile content concentration of the total reactive components is 10 to 40% by weight, preferably 15 to 35% by weight.

[0043] Examples of polymerization initiators include persulfates such as ammonium persulfate, potassium persulfate, and sodium persulfate; azo compounds such as 2,2'-azobis(2-amidinopropane)hydrochloride, and 2,2'-azobis[2(2-imidazolin-2-yl)propane]hydrochloride; and hydrogen peroxide. These may be used alone or two or more thereof may be used in combination. Among these, in order for solution polymerization to proceed sufficiently, ammonium persulfate, potassium persulfate, and 2,2'-azobis(2-amidinopropane)hydrochloride are preferable. In addition, a method of adding a polymerization initiator may be appropriately selected from batch addition, divided addition, continuous dropwise addition, and the like. The content of the polymerization initiator is generally about 0.001 to 5 parts by weight,

preferably about 0.01 to 2 parts by weight with respect to 100 parts by weight of the total reactive components.

[0044] Examples of the polymerization methods include a method using only a dropping polymerization method, a method using only a simultaneous polymerization method (putting mixed monomer solutions together), and a method combining a simultaneous polymerization method and a dropping polymerization method.

[0045] As for the reaction conditions, the temperature is preferably 40 to 100°C, and more preferably 50 to 100°C. The time is preferably 1 to 10 hours, and more preferably 1 to 8 hours.

[0046] The surface paper strength enhancer of the present invention may be combined with additives such as antifoaming agents, preservatives, chelating agents, water-soluble aluminum compounds, and urea; and starches such as oxidized starch, phosphate esterified starch, APS modified starch, enzyme modified starch, cationized starch, and amphoteric starch.

[0047] Regarding the physical properties of the surface paper strength enhancer of the present invention, the viscosity at 25°C of a solution of the surface paper strength enhancer at a non-volatile content concentration of 20% by weight is 100 to 5,000 mPa·s. The viscosity herein is a value measured with a B-type viscometer (Brookfield viscometer). By exhibiting such viscosity, the surface paper strength enhancer tends to exhibit an excellent paper strength enhancing effect. From the same standpoint, the viscosity is preferably 150 to 4,900 mPa·s, and more preferably 200 to 4,800 mPa·s.

[0048] As for other physical properties, a specific turbidity value (unit: NTU) at pH 5 to 8 of an aqueous solution containing 1% by weight of the surface paper strength enhancer and 0.5% by weight of aluminum sulfate in terms of non-volatile content concentration is used.

[0049] The turbidity is the degree of turbidity, and is a value obtained by measuring 180-degree scattered light using 900 nm infrared light using ANALITE NEPHELOMETER 152 (commercially available from Mc Van Instruments). The measured value is a relative evaluation value with respect to a standard substance (formazin standard solution 400 NTU, commercially available from Wako Pure Chemical Industries, Ltd.).

[0050] The turbidity of the present invention is measured with an aqueous solution containing the surface paper strength enhancer and aluminum sulfate each at a predetermined concentration, and a maximum turbidity value (X) and a minimum turbidity value (Y) are read from the turbidity values in a pH range of 5 to 8, and the maximum turbidity value (X) and the difference between the maximum turbidity value and the minimum turbidity value (X-Y) are used as physical property values.

[0051] As a method for preparing the aqueous solution, an aluminum sulfate aqueous solution previously diluted to a predetermined concentration with deionized water may be mixed with the surface paper strength enhancer, or the surface paper strength enhancer and aluminum sulfate may each be diluted to a predetermined concentration with deionized water and then mixed. Regarding the turbidity values, in the case of an aluminum sulfate aqueous solution alone, as the pH is increased, polymerization of the aluminum compound proceeds, showing a high turbidity value at pH 5 to 8, and the cloudiness is maintained up to pH 10 (FIG. 1 shows the change in turbidity of an aluminum sulfate aqueous solution at a non-volatile content concentration of 0.5% by weight). On the other hand, mixing the surface paper strength enhancer with aluminum sulfate suppresses the polymerization of the aluminum compound, and the turbidity value becomes smaller compared to aluminum sulfate alone, and as a result, it is presumed that the surface paper strength enhancer of the present invention tends to exhibit a high paper strength enhancing effect.

[0052] Regarding the maximum turbidity value (X), from the standpoint that the surface paper strength enhancer tends to exhibit an excellent paper strength enhancing effect, $10 \leq X \leq 200$ (the maximum turbidity value is 10 or more and 200 or less) is preferable, $25 \leq X \leq 190$ (the maximum turbidity value is 25 or more and 190 or less) is more preferable, and $35 \leq X \leq 180$ (the maximum turbidity value is 35 or more and 180 or less) is further preferable.

[0053] Regarding the difference between the maximum turbidity value and the minimum turbidity value (X-Y), from the standpoint that the surface paper strength enhancer tends to exhibit an excellent paper strength enhancing effect, $X-Y \leq 50$ (the difference between the maximum turbidity value and the minimum turbidity value is 50 or less) is preferable, $3 \leq X-Y \leq 45$ (the difference between the maximum turbidity value and the minimum turbidity value is 3 or more and 45 or less) is more preferable, and $5 \leq X-Y \leq 40$ (the difference between the maximum turbidity value and the minimum turbidity value is 5 or more and 40 or less) is further preferable.

[0054] The non-volatile content concentration of the surface paper strength enhancer is preferably 10 to 40% by weight, and more preferably 15 to 30% by weight.

[0055] The coating liquid of the present invention includes the surface paper strength enhancer, and the undiluted solution of the surface paper strength enhancer may be used as is, but from the standpoint of being able to uniformly apply the coating liquid to the surface of the base paper and facilitating penetration into the interior thereof, it is preferable to dilute the coating liquid with water or the like to a solid content concentration of 0.1 to 15% by weight.

[0056] Regarding the physical properties of the coating liquid of the present invention, for example, the viscosity measured with a B-type viscometer at a temperature of 50°C of a 5% by weight solid content aqueous solution is ordinarily 50 mPa·s or less, and preferably 40 mPa·s or less.

[0057] Various publicly known additives may also be incorporated into the coating liquid of the present invention as

needed. Examples of the additives include sizing agents such as rosin-based sizing agents, alkyl ketene dimer-based sizing agents, and polymer-based sizing agents; starches such as oxidized starch, phosphate esterified starch, APS modified starch, enzyme modified starch, cationized starch, and amphoteric starch; celluloses such as carboxymethyl cellulose; paper strength enhancers such as water-soluble polymers including polyvinyl alcohols and sodium alginate; anti-slip agents, preservatives, rust inhibitors, pH adjusters, antifoaming agents, thickeners, fillers, antioxidants, water-resistant agents, film-forming aids, pigments, and dyes.

[0058] The method for producing a coated paper of the present invention includes a step of applying the coating liquid of the present invention to a surface of a base paper and drying the base paper.

[0059] Examples of the base paper include PPC paper, inkjet recording paper, form paper, paperboard, liner, fluting, newsprint, base paper for coating, thermal paper, and the like. Among these, it is preferable to apply coatings to paperboard from the standpoint that the surface paper strength enhancer penetrates well into the base paper and exhibits an excellent paper strength enhancing effect. Various chemicals such as fillers, internal sizing agents, and paper strength enhancers may be added to the base paper, but in order to exhibit the paper strength enhancing effect in the present invention, it is preferable to incorporate an aluminum compound such as aluminum sulfate or polyaluminum chloride into the base paper. As a method therefor, an aluminum compound may be added to the raw material pulp constituting the base paper, or an aluminum compound may be applied to the surface of the obtained base paper.

[0060] The addition rate in the case where the aluminum compound is internally added is preferably about 0.3 to 7% by weight, and more preferably 0.5 to 5% by weight, relative to the solid content weight of the raw material pulp, from the standpoint of interaction with the aluminum compound contained in the base paper upon application of the coating liquid. Moreover, the coating amount in the case of applying to the surface is also preferably about 0.05 to 5 g/m², and more preferably about 0.1 to 4 g/m², from the same standpoint.

[0061] Examples of a coater for applying coatings to the base paper include a bar coater, a knife coater, an air knife coater, a calender, a gate roll coater, a blade coater, a 2-roll size press, a film press, and rod metering and the like.

[0062] The coating amount (solid content) of the coating liquid is preferably about 0.001 to 3 g/m², and more preferably about 0.005 to 2 g/m², from the standpoint of exhibiting an excellent paper strength enhancing effect.

[0063] The conditions for drying the paper after coating include a temperature of preferably 50 to 150°C, and more preferably 60 to 140°C. The drying time is preferably 1 to 10 minutes, and more preferably 2 to 8 minutes.

Examples

[0064] Hereinafter, the present invention will be described with reference to examples, but the present invention is not limited thereto. Unless otherwise specified, "parts" and "%" in examples and comparative examples are based on weight.

[0065] The following reactive components and polymerization initiators are indicated by the following abbreviations.

AM: acrylamide
 AGA: 2-acrylamido-N-glycolic acid
 Gly: glyoxylic acid
 SMAS: sodium methallyl sulfonate
 DMAA: N,N-dimethylacrylamide
 MBAA: N,N'-methylenebisacrylamide
 IA: itaconic acid
 AA: acrylic acid
 APS: ammonium persulfate

<Viscosity>

[0066] The polymer (A) was diluted with deionized water to a non-volatile content concentration of 20%, adjusted to a temperature of 25°C, and then the viscosity was measured using a B-type viscometer (manufactured by Toki Sangyo Co., Ltd.).

Example 1

[0067] Deionized water (523 parts) was inserted into a reaction device including a stirrer, a thermometer, a reflux cooling pipe, a nitrogen gas instruction pipe, and two dropping funnels, and after removing oxygen in the reaction system by passing nitrogen gas through, the reaction system was heated to 85°C. Separately, a 50% AM aqueous solution (771.6 parts), AGA (0.8 parts), SMAS (26.9 parts), DMAA (5.6 parts), MBAA (0.9 parts), and deionized water (299 parts) were prepared in dropping funnel (1) so that the non-volatile content concentration in dropping funnel (1)

was 38%. In addition, 1.5 parts of APS and 150 parts of deionized water were put into a dropping funnel (2). Next, dropwise addition was performed into the reaction device over 3 hours from the dropping funnels (1) and (2). After dropwise addition was completed, 0.5 parts of APS (0.5 parts) and 10 parts of deionized water were added, and at the point at which the estimated viscosity measured by a B-type viscometer reached approximately 4,000 mPa·s (at a temperature of 25°C, converted to a non-volatile content concentration of 20%), the polymerization was terminated and the reaction mixture was cooled to obtain polymer (A-1). The viscosity of the obtained polymer (A-1) is shown in Table 1 (the same applies hereinafter).

Examples 2 to 9, Examples 11 to 14, Comparative Examples 1 to 6

[0068] The reactive components and amounts used were changed to those shown in Table 1, and the procedure was carried out in the same manner as in Example 1 to obtain polymer (A-2) to polymer (A-9), polymer (A-11) to polymer (A-14), and polymer (B-1) to polymer (B-6), respectively. In Comparative Example 3 (polymer (B-3)) and Comparative Example 6 (polymer (B-6)), gelation occurred during polymerization, and therefore the following evaluations were not performed.

Example 10

[0069] Deionized water (523 parts) was inserted into a reaction device similar to that of Example 1, and after removing oxygen in the reaction system by passing nitrogen gas through, the reaction system was heated to 85°C. Separately, a 50% AM aqueous solution (680.4 parts), a 50% Gly aqueous solution (24.6 parts), SMAS (26.3 parts), DMAA (41.1 parts), MBAA (0.2 parts), and deionized water (333 parts) were prepared in dropping funnel (1) so that the non-volatile content concentration in dropping funnel (1) was 38%. Moreover, APS (1.5 parts) and deionized water (150 parts) were prepared in dropping funnel (2). Next, the contents were added dropwise from dropping funnel (1) and dropping funnel (2) into the reaction device over 3 hours. After completion of the dropwise addition, APS (0.5 parts) and deionized water (10 parts) were inserted, and at the point at which the estimated viscosity measured by a B-type viscometer reached approximately 4,900 mPa·s (at a temperature of 25°C, converted to a non-volatile content concentration of 20%), the polymerization was terminated and the reaction mixture was cooled to obtain polymer (A-10).

<Preparation of Aqueous Solution for Turbidity Measurement>

[0070] Aluminum sulfate·14 to 18 hydrate (manufactured by Wako Pure Chemical Industries, Ltd.) (10 parts) and deionized water (990 parts) were mixed in advance to prepare an aluminum sulfate aqueous solution having a solid content concentration of 1%. Next, polymer (A-1) (5 parts, non-volatile content: 1 part) and deionized water (45 parts) were mixed, and then the aluminum sulfate aqueous solution (50 parts) was added to prepare an aqueous solution for turbidity measurement (non-volatile content concentration - polymer (A-1): 1%, aluminum sulfate: 0.5%). Moreover, aqueous solutions were prepared in the same manner for polymer (A-2) to polymer (A-14), polymer (B-1), polymer (B-2), polymer (B-4), and polymer (B-5).

<Turbidity>

[0071] The aqueous solution was adjusted to a temperature of 25°C and stirred at 500 rpm with a stirrer. Using a turbidimeter (device name: "ANALITE NEPHELOMETER 152", manufactured by McVan Instruments), a 1% sodium hydroxide aqueous solution was gradually added dropwise to raise the pH, or a 1% sulfuric acid aqueous solution was gradually added dropwise to lower the pH, so that the pH changed by 0.1 at a time. The maximum turbidity value (X) and minimum turbidity value (Y) at pH 5 to 8 were read from the resulting turbidity graph, and the difference between the maximum value and the minimum value was calculated. In cases where the turbidity value was not stable, the measurement was waited until it stabilized, and the value at the point of stabilization was taken as the turbidity value. The turbidity value is a relative value based on a formazin standard solution (400 NTU, manufactured by Wako Pure Chemical Industries, Ltd.) as a reference material, and was obtained by measuring scattered light at 180 degrees using infrared light at 900 nm. Moreover, a turbidity graph for the cases in which the surface paper strength enhancers of Example 3 and Comparative Example 2 were used is shown in FIG. 1. The results are shown in Table 1.

[Table 1]

	Polymer	Reactive component (mol%)							viscosity <mPa·s>	Turbidity (NTU)		
		AM	AGA	Gly	SMAS	DMAA	MBAA	IA	AA	Minimum value Y	Maximum value X	Difference X-Y
Example 1	A-1	95.8	0.1	-	3.0	1.0	0.10	-	-	155	170	15
Example 2	A-2	95.87	0.03	-	3.0	1.0	0.10	-	-	140	185	45
Example 3	A-3	92.9	3.0	-	3.0	1.0	0.10	-	-	93	110	17
Example 4	A-4	87.9	8.0	-	3.0	1.0	0.10	-	-	50	60	10
Example 5	A-5	77.9	14.0	-	3.0	5.0	0.10	-	-	35	39	4
Example 6	A-6	95.3	3.0	-	0.60	1.0	0.10	-	-	115	130	15
Example 7	A-7	89.9	3.0	-	6.0	1.0	0.10	-	-	95	108	11
Example 8	A-8	80.9	3.0	-	9.5	6.5	0.10	-	-	82	90	8
Example 9	A-9	94.0	3.0	-	3.0	-	0.01	-	-	85	93	8
Example 10	A-10	86.5	-	3	3.0	7.5	0.02	-	-	124	135	11
Example 11	A-11	91.9	3.0	-	3.0	1.0	0.10	1.0	-	125	148	23
Example 12	A-12	86.9	3.0	-	3.0	2.0	0.10	5.0	-	150	185	35
Example 13	A-13	91.9	3.0	-	3.0	1.0	0.10	-	1.0	120	132	12
Example 14	A-14	90.4	3.0	-	3.0	1.5	0.10	1.0	1.0	145	174	29
Comparative Example 1	B-1	98.6	-	-	0.30	1.0	0.10	-	-	193	220	27
Comparative Example 2	B-2	92.9	-	-	3.0	1.0	0.10	3.0	-	158	317	159
Comparative Example 3	B-3	95.9	3.0	-	-	1.0	0.10	-	-	gelation during polymerization		
Comparative Example 4	B-4	94.0	3.0	-	3.0	-	-	-	-	78	88	11
Comparative Example 5	B-5	82.9	3.0	-	130	1.0	0.10	-	-	83	97	14
Comparative Example 6	B-6	83.9	3.0	-	3.0	10.0	0.10	-	-	gelation during polymerization		

<Preparation of Coating Liquid>

[0072] Polymer (A-1) to polymer (A-14), polymer (B-1), polymer (B-2), polymer (B-4), and polymer (B-5) were diluted with deionized water to a non-volatile content concentration of 5% to prepare coating liquids.

<Preparation of Base Paper>

[0073] Recycle corrugated cardboard was beaten with a Niagara-type beater, and aluminum sulfate·14 to 18 hydrate was added at 1.0% relative to the non-volatile content weight of the raw material pulp to a raw material pulp adjusted to a Canadian Standard Freeness (C.S.F) of 350 ml, thereby obtaining a slurry. The papermaking pH at that time was 6.5. Subsequently, the slurry was dewatered with a Tappi sheet machine, pressed at 5 kg/cm² for 2 minutes, dried with a rotary dryer at 105°C for 4 minutes, and conditioned for 24 hours under conditions of a temperature of 23°C and a humidity of 50% to prepare a base paper.

Evaluation Examples 1 to 14, Comparative Evaluation Examples 1 to 4

[0074] Each coating liquid preheated to 50°C was applied to both sides of the base paper using a bar coater. The coated paper was obtained by drying for 1 minute with a rotary drum dryer at 105°C. In this evaluation, the coating liquid was applied so that the adhesion amount (non-volatile content) of the coating liquid was 1.5 g/m².

<Bursting Strength>

[0075] The specific burst strength (kPa·m²/g) was measured using the paper obtained above according to JIS P 8131. The results are shown in Table 2.

<Compressive Strength>

[0076] Using each coated paper, the specific compressive strength (N·m²/g) was measured in accordance with JIS P 8126. The results are shown in Table 2.

[Table 2]

	Polymer	Specific bursting strength (kP·m ² /g)	Specific compressive strength (N·m ² /g)
Evaluation Example 1	A-1	2.77	166
Evaluation Example 2	A-2	2.70	162
Evaluation Example 3	A-3	2.85	170
Evaluation Example 4	A-4	2.87	173
Evaluation Example 5	A-5	2.87	174
Evaluation Example 6	A-6	2.84	172
Evaluation Example 7	A-7	2.81	169
Evaluation Example 8	A-8	2.78	167
Evaluation Example 9	A-9	2.79	168
Evaluation Example 10	A-10	2.84	170
Evaluation Example 11	A-11	2.83	171
Evaluation Example 12	A-12	2.81	169
Evaluation Example 13	A-13	2.84	171
Evaluation Example 14	A-14	2.83	171
Comparative Evaluation Example 1	B-1	2.56	151
Comparative Evaluation Example 2	B-2	2.60	156
Comparative Evaluation Example 3	B-4	2.59	153

(continued)

	Polymer	Specific bursting strength (kP·m ² /g)	Specific compressive strength (N·m ² /g)
5 Comparative Evaluation Example 4	B-5	2.62	159

Claims

- 10 1. A surface paper strength enhancer containing a polymer (A) comprising, as reactive components, a (meth)acrylamide (a1), a (meth)acrylamide (a2) having a carboxy group, an ethylenically unsaturated monomer (a3) having a sulfo group, and a crosslinkable monomer (a4),
 15 wherein a solution of the surface paper strength enhancer having a non-volatile content concentration of 20% by weight has a viscosity of 100 to 5,000 mPa·s at a temperature of 25°C.
2. The surface paper strength enhancer according to claim 1, wherein the reactive components further contain an ethylenically unsaturated monomer (a5) having a carboxy group other than the component (a2).
- 20 3. The surface paper strength enhancer according to claim 1, wherein, with total reactive components being 100 mol%, the component (a1) is 72 to 97 mol%, the component (a2) is 0.01 to 15 mol%, the component (a3) is 0.4 to 10 mol%, and the component (a4) is 0.001 to 8 mol%.
- 25 4. The surface paper strength enhancer according to claim 1, wherein, in an aqueous solution containing the surface paper strength enhancer at 1% by weight and aluminum sulfate at 0.5% by weight in terms of non-volatile content concentration, when a maximum turbidity value at pH 5 to 8 is X and a minimum turbidity value is Y, $10 \leq X \leq 200$ and $X - Y \leq 50$ are satisfied.
5. A coating liquid containing the surface paper strength enhancer according to any one of claims 1 to 4.
- 30 6. A method for producing paper, comprising a step of applying the coating liquid according to claim 5 to a surface of a base paper and drying the base paper.
- 35 7. The method for producing paper according to claim 6, wherein the base paper comprises an aluminum compound.

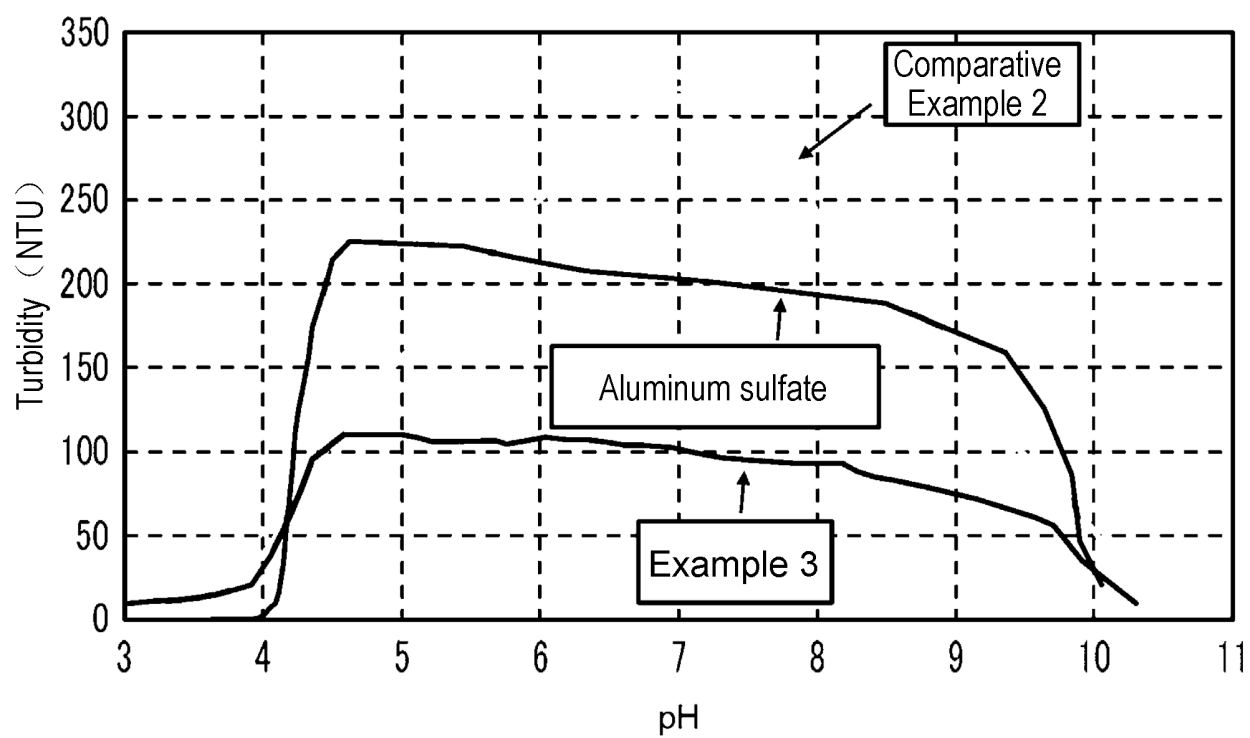


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/041407

A. CLASSIFICATION OF SUBJECT MATTER

D21H 21/18(2006.01)i; **D21H 17/37**(2006.01)i; **D21H 19/20**(2006.01)i
 FI: D21H21/18; D21H17/37; D21H19/20 A

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H21/18; D21H17/37; D21H19/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 6977915 B1 (SEIKO PMC CORPORATION) 08 December 2021 (2021-12-08) paragraphs [0012]-[0073], fig. 1-2, tables 1-5	1-2, 5
Y		6-7
A		3-4
Y	JP 2023-88732 A (MITSUBISHI PAPER MILLS LTD.) 27 June 2023 (2023-06-27) paragraphs [0014]-[0022]	6-7
A		1-5

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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“&” document member of the same patent family

Date of the actual completion of the international search

12 December 2024

Date of mailing of the international search report

24 December 2024

Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2024/041407

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
JP	6977915	B1	08 December 2021	WO	2021/166898	A1	
				CN	113574224	A	
				KR	10-2022-0138857	A	
JP	2023-88732	A	27 June 2023	(Family: none)			

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2019173257 A [0005]