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(54) **Paper strengthening agent and paper strengthening method**

(57) There is provided a paper strengthening agent comprising a polymer dispersion manufactured by polymerizing a monomer containing (meth)acrylic acid in an aqueous solution and precipitating the produced polymer as fine particles, and which is added to a paper layer after a paper layer is formed, wherein (1) the concentration of the (meth)acrylic acid (co)polymer in said polymer dispersion is at least 5 wt%, (2) the average particle diameter of the (meth)acrylic acid (co)polymer particles in said polymer dispersion is 1 to 100  $\mu\text{m}$ , (3) the viscosity of said polymer dispersion is 30 to 5000  $\text{mPa} \cdot \text{s}$  immediately after and one month after the production, (4) the polymer particles can be recognized when said polymer dispersion is diluted 10 times with distilled water and the diluted dispersion is magnified by a factor of 400 and observed with a microscope, and (5) when the pH of said diluted dispersion is adjusted to 7.0 by adding alkali, said polymer particles are dissolved to form an aqueous solution. The paper strengthening agent prepared in this manner allows to obtain paper having increased paper strength by diluting with water, coating or impregnating onto a dry paper surface or wet paper surface, and drying the treated paper.

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## Description

[0001] The present invention relates to a paper strengthening agent comprising a dispersion of fine water-insoluble polymer particles manufactured by polymerizing a monomer containing (meth)acrylic acid in an aqueous solution and precipitating the produced polymer, which is added to a paper layer after a paper layer is formed in a paper making process and relates to a paper strengthening method wherein a low-viscosity polymer dispersion prepared by diluting the present paper strengthening agent with water is impregnated into paper by spraying or coating.

[0002] The Laid-Open Japanese Patent Application No. Sho 62-20511 discloses a method of obtaining a water-soluble polymer dispersion by polymerizing a monomer in an aqueous salt solution that dissolves the monomer and does not dissolve a formed polymer in the presence of a polymer electrolyte.

[0003] On the other hand, the Laid-open Japanese Patent Application No. Sho 60-185900 discloses a method for obtaining a dispersion of fine polymer particles by polymerizing acrylic acid with acrylamide in an aqueous salt solution that dissolves the monomers but does not dissolve the formed polymer. In this method, the fine particles can be obtained in the absence of any polymer electrolyte. The fine polymer particles obtained here are water-insoluble and dissolved in a solvent if the dispersion is neutralized. That is, it is a different technique from that proposed in the Laid-open Japanese Patent Application No. Sho 62-20511. However, the fine particles in the dispersion of acrylic acid-acrylamide copolymer agglomerate on standing resulting in curdling in the manner of bean curd, thereby having the disadvantage of being unable to be stored for long periods of time.

[0004] An object of the present invention is to increase bursting strength, ring crush strength and surface paper strength such as wax pic by efficiently impregnating a paper layer with a high molecular weight polymer.

[0005] Another object of the present invention is to increase the interlayer adhesive paper strength by adhering a high molecular weight polymer to a plurality of web surfaces.

[0006] The inventors of the present invention discovered that a dispersion of fine polymer particles having a low viscosity, good workability and excellent stability for preservation can be manufactured by polymerizing a monomer containing (meth)acrylic acid in the presence of a dispersibility retaining agent such as a cationic polymer electrolyte to precipitate the produced polymer. Moreover, during the course of various attempts to search for applications for this dispersion, the inventors of the present invention also discovered that said dispersion demonstrates outstanding effects such as paper strengthening by coating said dispersion onto dry paper with a size press, gate roll coater or blade coater and so forth, paper strengthening by spray impregnating said dispersion into wet paper on a wire part, and interlayer adhesion paper strengthening by adhering a polymer of said dispersion onto a plurality of web surfaces, thereby leading to completion of the present invention.

[0007] A first aspect of the present invention is to provide a paper strengthening agent substantially comprising a polymer dispersion manufactured by polymerizing a monomer containing (meth)acrylic acid in an aqueous solution and precipitating the produced polymer as fine particles, and which is added to a paper layer after a paper layer is formed, wherein

- (1) the concentration of the (meth)acrylic acid (co)polymer in the polymer dispersion is at least 5 wt%,
- (2) the average particle diameter of the (meth)acrylic acid (co)polymer particles in the polymer dispersion is 1 to 100  $\mu\text{m}$ ,
- (3) the viscosity of the polymer dispersion is 30 to 5000  $\text{mPa} \cdot \text{s}$  immediately after and one month after the production,
- (4) the polymer particles can be recognized when the polymer dispersion is diluted 10 times with distilled water and the diluted dispersion is magnified by a factor of 400 and observed with a microscope, and
- (5) when the pH of the diluted dispersion is adjusted to 7.0 by adding an alkali, the polymer particles are dissolved to form an aqueous solution.

[0008] A second aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the polymer dispersion is polymerized and precipitated in the presence of a dispersibility retaining agent comprising a polyvalent electrolyte.

[0009] A third aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the dispersibility retaining agent is one selected from a cationic polymer electrolyte, a surface active agent having a polyvalent cationic hydrophilic group and a hydrophobic group, and a mixture thereof.

[0010] A fourth aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the weight ratio of the monomer containing (meth)acrylic acid in an aqueous solution to the dispersibility retaining agent is 100:1 to 10:1.

[0011] A fifth aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the viscosity of said polymer dispersion is 30 to 1500  $\text{mPa} \cdot \text{s}$  immediately

after and one month after the production.

**[0012]** A sixth aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the dispersibility retaining agent is dimethyldiallylammonium chloride (co)polymer.

5 **[0013]** A seventh aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the dispersibility retaining agent is an alkyl group-substituted and/or an aralkyl group-substituted polyethylenepolyamine.

**[0014]** An eighth aspect of the present invention is to provide a paper strengthening agent characterized in that, in the above-mentioned paper strengthening agent, the dispersibility retaining agent is an alkyl group having at least 5 carbon atoms-substituted and/or an aralkyl group-substituted pentaethylenehexamine.

**[0015]** A ninth aspect of the present invention is to provide a paper strengthening method comprising the steps of: diluting the above-mentioned paper strengthening agent with water to prepare a diluted dispersion, coating or impregnating said diluted dispersion onto a dry paper, and drying the treated dry paper.

15 **[0016]** A tenth aspect of the present invention is to provide a paper strengthening method wherein a diluted dispersion of the above-mentioned paper strengthening agent is impregnated into wet paper.

**[0017]** An eleventh aspect of the present invention is to provide a paper strengthening method wherein a diluted dispersion of the above-mentioned paper strengthening agent is spray impregnated into wet paper.

**[0018]** A twelfth aspect of the present invention is to provide a paper strengthening method wherein the wet paper in the above method is of a single layer.

20 **[0019]** A thirteenth aspect of the present invention is to provide a method of preventing interlayer separation comprising the steps of spraying a diluted dispersion of the above-mentioned paper strengthening agent onto a web surface to prepare a plurality of webs having a polymer adhered to surfaces thereof, and pressing the surfaces of said webs so as to be superimposed followed by drying.

**[0020]** The monomer that contains (meth)acrylic acid used in the present invention is a mixture of 5 to 50 mol% of acrylic acid, methacrylic acid or a mixture thereof, and itaconic acid and/or acryloylaminoisobutyl sulfonic acid and so forth over a range that does not lower the degree of polymerization or have a detrimental effect on solubility; and, 50 to 95 mol% of one type of nonionic monomer selected from the group consisting of (meth)acrylamide, (meth)acrylonitrile, N-vinylcarboxylic amide, N-isopropyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, methyl(meth)acrylate, hydroxyethyl(meth)acrylate, vinylmethylether, vinylacetate, styrene and a mixture thereof.

30 **[0021]** Cationic monomer can be polymerized as a component of the monomer containing (meth)acrylic acid over the range in which water insolubility of the resulted polymer can be secured when diluting with distilled water.

**[0022]** Among them, a monomer composition that contains 5 to 50 mol% of (meth)acrylic acid, 50 to 95 mol% of (meth)acrylamide and 0 to 50 mol% of (meth)acrylonitrile is most preferable.

**[0023]** It is preferable to carry out polymerization in the presence of a dispersibility retaining agent in order to obtain a polymer dispersion in the present invention. Examples of the dispersibility retaining agent comprising a cationic polymer electrolyte used in the present invention are (co)polymers of salts or quaternary products of dialkylaminoalkyl(meth)acrylate, (co)polymers of salts or quaternary products of dialkylaminoalkyl(meth)acrylamide, and (co)polymers of dialkyldiallylammonium salt.

40 **[0024]** Examples of the salts or quaternary products of dialkylaminoalkyl(meth)acrylate include dimethylaminoethyl(meth)acrylate hydrochloride and acryloyloxyethyltrimethylammonium chloride. Also, examples of the salts or quaternary products of the dialkylaminoalkyl(meth)acrylamide include hydrochlorides or methylated products of dialkylaminopropyl(meth)acrylamide. An example of dialkyldiallylammonium salt is dimethyldiallylammonium chloride.

**[0025]** Not only one type, but also a mixture of two or more types of cationic monomers that form said cationic water-soluble polymer can be used.

45 **[0026]** The cationic water-soluble polymer may be a homopolymer or a copolymer with a nonionic monomer such as acrylamide.

**[0027]** A particularly preferable cationic water-soluble polymer is dimethyldiallylammonium chloride (co)polymer.

**[0028]** An example of a dispersibility retaining agent comprising a surface active agent having a polyvalent cationic hydrophilic group and a hydrophobic group used in the present invention is a substituted polyethylenepolyamine in which at least one hydrogen atom at a nitrogen atom thereof is substituted by an alkyl group and/or an aralkyl group. An alkyl group-substituted product of pentaethylenehexamine having at least 5 carbon atoms in said alkyl group is effective.

**[0029]** The weight ratio of the monomer that contains (meth)acrylic acid to the dispersibility retaining agent is preferably 100:1 to 10:1. If the amount of the dispersibility retaining agent is too small, the dispersion curds into the form of bean curd. On the other hand, excessive addition of dispersibility retaining agent is economically meaningless.

**[0030]** The dispersibility retaining agent according to present invention may be a sole compound or a mixture thereof.

**[0031]** As a result of adding dispersibility retaining agent within said range, the viscosity of the polymer dispersion is maintained within the range of 30 to 5000 mPa · s immediately after and one month after the production, and is stable

for a long time.

[0032] A product having a viscosity of 30 to 1500 mPa · s is preferable in terms of handling when considering convenience during use.

[0033] Since the polymer dispersion of the present invention uses a polyvalent cationic compound as the dispersibility retaining agent, the surface charge of the polymer particles is considered to be cationic, and it can also be mixed with an aqueous solution of a water-soluble cationic polymer and an aqueous dispersion.

[0034] An aqueous salt solution may also be used in the present invention for the purpose of promoting polymer precipitation. Examples of the salt that forms said aqueous salt solution include alkaline metal salts such as sodium salt and potassium salt, and ammonium salts such as ammonium chloride, ammonium sulfate and ammonium nitrate. The concentration and pH of said aqueous salt solution must be such that the monomers containing (meth)acrylic acid dissolve, while the polymer that is formed does not. In contrast, it is necessary that the dispersibility retaining agent that is also present be soluble in said aqueous salt solution.

[0035] The (meth)acrylic acid (co)polymer dispersion and the dispersibility retaining agent in the present invention can respectively be obtained by dissolving monomer(s) in an aqueous medium under nitrogen atmosphere without oxygen, and radical polymerizing the monomer(s) by adding a water-soluble azo type polymerization initiator such as 2,2'-azobis(2-amidinopropane) hydrochloride or a water-soluble redox type polymerization initiator using such as both ammonium persulfate and sodium hydrogen sulfite.

[0036] Temperature of the polymerization system can be selected arbitrarily depending on the property of the polymerization initiator used within the range of 0 to 100°C. For adjusting the molecular weight of the polymer obtained, a chain transfer agent such as isopropylalcohol or mercaptan can be added and used by arbitrary selection in the same manner as ordinary radical polymerization. At the time of preparing the (meth)acrylic acid (co)polymer dispersion, stirring at a peripheral speed of a stirrer of at least 1 meter/min must be performed for smoothening the precipitation of fine polymer particles. There is no upper limit of the stirring speed and any stirring conditions can be selected provided that the contents do not overflow from the equipment. Although preparation of the dispersibility retaining agent is generally performed by the stationary polymerization in an aqueous solution, the polymerization therefor in the present invention is preferably performed under stirring from the viewpoint of the homogenization of products.

[0037] The polymer concentration in the dispersion of the present invention is high or at least 5 wt% and is normally from 5 wt% to about 40 wt%.

[0038] Although the dispersion of the present invention contains a high concentration of formed polymer, the viscosity of the dispersion is low, normally low at 30 to 5000 mPa · s, and preferably 30 to 1500 mPa · s, because the polymer is stably dispersed in a dispersion medium in a state of fine particles. Therefore, as its characteristics, the polymer dispersion can flow easily and can be handled very easily.

[0039] The polymer particles in the dispersion of the present invention can be recognized in a non-diluted state and in a state diluted 10 times with distilled water when it is magnified by a factor of 400 with an optical microscope. At this time, the average particle diameter of the polymer particles is normally 1 to 100 μm, preferably 2 to 50 μm, and more preferably 2 to 30 μm. When the average particle diameter of the polymer particles exceeds 100 μm, since the particles tend to precipitate easily, settling stability deteriorates. Moreover, solubility also deteriorates at the time of use due to the large size of the polymer particles even when mixed with water, thus requiring a long time to completely dissolve the polymer. On the contrary, the dispersion of the present invention has excellent settling stability and any trouble such as adherence of particles to each other thereby creating masses does not occur even during storage at the normal temperature. In addition, the solubility thereof in water during use is extremely good.

[0040] The molecular weight of the polymer in the dispersion of the present invention is not specially limited. If the dispersion of the present invention is expressed by the solution viscosity when dissolved in 2 wt% of aqueous salt solution of ammonium sulfate (viscosity measured at 25°C by using a Brookfield viscometer) in such a manner that the concentration of the polymer becomes 0.5 wt%, it is normally in the range of 5 to 200 mPa · s. Also, the dispersion of the present invention hardly has any change in viscosity with time even after storage for 1 month.

[0041] When the dispersion of the present invention is diluted 10 times, the polymer particles can be recognized with a microscope and when an alkali is added to the dispersion to adjust the pH of the dispersion to 7.0, said polymer particles are dissolved to form an aqueous solution. That is, the dispersion of the present invention can be said to be a dispersion of the fine particles of water-insoluble polymer.

[0042] In the present invention, paper strengthening effects are obtained by coating or impregnating an aqueous diluted dispersion of said paper strengthening agent onto a dry paper or wet paper surface and then drying.

[0043] In the paper strengthening method of the present invention, the paper strengthening agent can be used in combination with another wet end chemical, for example a retention aid for fillers or a drainage aid. More specifically, an aqueous solution of cationic starch, cationic polyacrylamide or other wet end paper strengthening agent and so forth is added and mixed with a paper material, and spraying a diluted aqueous dispersion of the paper strengthening agent according to the present invention onto wet paper at each intermediate stage of formation of the sheet, namely before the suction part or on the suction part, with a wire to impregnate said diluted aqueous dispersion into the paper.

**[0044]** In another embodiment according to the present invention, after drying manufactured paper, polymer is impregnated onto the surface and inside the paper by coating a diluted aqueous dispersion of the paper strengthening agent of the present invention onto the resulting dry paper by a size press, gate roll coater or blade coater and so forth.

**[0045]** Nearly the entire amount of polymer coated according to said method is retained within the paper, namely within the pulp sheet. Due to adhesion of pulp fibers and so forth, it is possible to increase not only surface paper strength, but also bursting strength and ring crush strength.

**[0046]** Paper to which the paper strengthening agent is added for these non-wet ends is frequently used in printing paper, recording paper and PPC paper (i.e. paper for plan paper copy), and the sheets are typically single layer.

**[0047]** In contrast, in the production of cardboard, a plurality of webs are typically combined with each other. By spraying a diluted aqueous dispersion of the paper strengthening agent of the present invention onto a web surface to prepare a plurality of webs adhered with polymer on the surface, and drying after pressing so as to overlap the surfaces of said webs, the strength of the paper, such as the interlayer adhesive paper strength of a plurality of laminated sheets of paper, can be increased making it possible to prevent interlayer separation.

**[0048]** Furthermore, conventional interlayer separation preventive agents such as starch, modified starch, casein and galactomannan may be also be used in the paper strengthening agent of the present invention.

**[0049]** The present invention is characterized in that the polymer comprising a water-soluble monomer containing (meth)acrylate is not used.

**[0050]** (Meth)acrylic (co)polymer is refractory and has a low viscosity even though the molecular weight is high, enabling even highly concentrated diluted aqueous dispersions to be coated onto a surface easily.

**[0051]** According to the present invention, a high molecular weight polymer can be efficiently coated in a water-insoluble state. Since the pH rises when the coated polymer is impregnated into paper, a portion of the polymer becomes water-soluble and transforms into a paste-like substance. Consequently, it is expected to function as an adhesive.

**[0052]** When considering the properties as a coating agent, there is no occurrence of decay in comparison with starch, and there are no increases in viscosity in comparison with an aqueous solution of (meth)acrylate (co)polymer.

Thus, there is no difficulty in spray coating onto wet paper and there is no occurrence of uneven coating of dry paper surfaces.

**[0053]** In the method of the present invention, the polymer dispersion is sprayed or coated onto the surface after diluting to a polymer concentration of 0.1 to 0.5 wt%.

**[0054]** The amount of polymer added to the paper by spraying or coating is a polymer net amount of 0.05 to 1.0 wt% per pulp SS (i.e. suspended solid), and preferably 0.1 to 0.5 wt%.

## EXAMPLES

**[0055]** Although the following provides a detailed explanation of the present invention through its examples, the present invention is not limited to the following.

### (PREPARATIVE EXAMPLE - 1)

**[0056]** In a reactor equipped with a stirrer, a nitrogen aeration pipe and a temperature controller, 10 parts of a monomer composition consisting of 15 mol% of acrylic acid, 55 mol% of acrylamide and 30 mol% of acrylonitrile, and 1 part of polydimethyldiallylammonium chloride as a dispersant (manufactured by CPS Co., trade name: Age Flock WT40HV) were dissolved in 89 parts of deionized water. Thereafter, as a polymerization initiator, 2,2'-azobis[2-(imidazoline-2-yl)propane] dihydrochloride (manufactured by Wako Pure Chemical Industries, Ltd., trade name: VA-044) was added. Under stirring, the polymerization was carried out for 20 hours at 35°C to obtain a polymer dispersion (pH 3) in which 5 to 50  $\mu\text{m}$  fine particles were dispersed. This dispersion is referred to as "Sample-1".

**[0057]** The viscosity of said polymer dispersion (Sample-1) was 1000 mPa · s, fine particles were recognized with a microscope even after diluting 10 times with distilled water, and the polymer was essentially confirmed to be water-insoluble. Sodium carbonate aqueous solution was mixed in said dispersion to adjust the pH of the dispersion to 7, after which the polymer was dissolved and the molecular weight thereof was determined from the intrinsic viscosity based on said aqueous solution.

### (PREPARATIVE EXAMPLE - 2)

**[0058]** The same operation as that of Preparative Example-1 was performed with the exception of using a monomer composition consisting of 30 mol% of acrylic acid, 45 mol% of acrylamide and 25 mol% of acrylonitrile to obtain a water-insoluble polymer dispersion. This dispersion is referred to as "Sample-2".

## (PREPARATIVE EXAMPLE - 3)

**[0059]** In a reactor equipped with a stirrer, a nitrogen aeration pipe and a temperature controller, 20 parts of a monomer composition consisting of 30 mol% of acrylic acid, 60 mol% of acrylamide and 10 mol% of acrylonitrile, and 1 part of polydimethyldiallylammonium chloride as a dispersant (manufactured by CPS Co., trade name: Age Flock WT40HV) were dissolved in 79 parts of an aqueous solution of sodium chloride having a concentration of 20 wt%. Thereafter, as a polymerization initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (manufactured by Wako Pure Chemical Industries, Ltd., trade name: V-50) was added. Under stirring, the polymerization was carried out for 10 hours at 53°C to obtain a polymer dispersion (pH 3) in which 10 to 20  $\mu\text{m}$  fine particles were dispersed in the aqueous salt solution. This dispersion is referred to as "Sample-3".

**[0060]** The viscosity of said polymer dispersion (Sample-3) was 500 mPa  $\cdot$  s or less, fine particles were recognized with a microscope even after diluting said dispersion 10 times with distilled water, and the polymer was essentially confirmed to be water-insoluble. Sodium carbonate aqueous solution was mixed in said dispersion to adjust the pH of the dispersion to 7, after which the polymer was dissolved and the molecular weight thereof was determined from the intrinsic viscosity based on said aqueous solution.

## (PREPARATIVE EXAMPLE - 4)

**[0061]** In a reactor equipped with a stirrer, a nitrogen aeration pipe and a temperature controller, 20 parts of a monomer composition consisting of 10 mol% of acrylic acid, 70 mol% of acrylamide and 20 mol% of acrylonitrile, and 1 part of a compound in which 3 moles of benzyl chloride were added to pentaethylenhexamine as a dispersant were dissolved in 79 parts of an aqueous solution of sodium chloride having a concentration of 20 wt%. Thereafter, as a polymerization initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (manufactured by Wako Pure Chemical Industries, Ltd., trade name: V-50) was added. Under stirring, the polymerization was carried out for 10 hours at 53°C to obtain a polymer dispersion (pH 3) in which 10 to 20  $\mu\text{m}$  fine particles were dispersed in the aqueous salt solution. This dispersion is referred to as "Sample-4".

**[0062]** The viscosity of said polymer dispersion (Sample-4) was 500 mPa  $\cdot$  s or less, fine particles were recognized in said dispersion with a microscope even after diluting 10 times with distilled water, and the polymer was essentially confirmed to be water-insoluble.

**[0063]** Sodium carbonate aqueous solution was mixed in said dispersion to adjust the pH of the dispersion to 7, after which the polymer was dissolved and the molecular weight thereof was determined from the intrinsic viscosity based on said aqueous solution.

**[0064]** Polymer characteristics of the Sample-1 to Sample-4 are shown in Table 1.

[TABLE 1]

No.	Sample Name	Monomers (mol%)			Molecular weight
		AAc	AAm	AN	
1	Sample-1	15	55	30	2,000,000
2	Sample-2	30	45	25	3,000,000
3	Sample-3	30	60	10	2,500,000
4	Sample-4	10	70	20	3,700,000
AAc: Acrylic acid AAm: Acrylamide AN: Acrylonitrile					

## (SURFACE COATING EFFECT TEST-1)

**[0065]** The polymer dispersion of the present example was diluted with pH 3.0 acidic water to prepare a diluted aqueous dispersion having a polymer concentration of 2.0%. This diluted dispersion was coated onto commercially available medium quality paper (basis weight: 55 g/m<sup>2</sup>, manufactured by Daishowa Paper Co., Ltd., neutral paper) using a coating rod and roll dried for 5 minutes at 105°C to obtain coated paper. The amounts of coated polymer were 0.1 g/m<sup>2</sup> and 0.2 g/m<sup>2</sup>. The results of bursting strength and surface strength tests are shown in Table 2.

[TABLE 2]

Results of Paper Strengthening Effect Test				
No.	Sample Name	Coated Amount (g/m <sup>2</sup> )	Burst Factor	Surface Strength WAX PIC
1	Sample-1	0.1	2.15	12A
2	Sample-1	0.2	2.24	13A
3	Sample-2	0.1	2.13	12A
4	Sample-3	0.1	2.12	12A
5	Sample-4	0.1	2.12	12A
6	Acidic starch only	0.5	1.50	11A
7	Non-coated	0	1.30	8A
WAX PIC: measured according to TAPPI (Technology Association of Pulp and Paper Industries) T459os-75				
BURSTING STRENGTH TEST: TAPPI T403om-85				

## (SURFACE COATING EFFECT TEST-2)

**[0066]** The polymer dispersion of the present example was diluted with pH 3.0 acidic water followed by the addition of acidic starch to prepare a coating liquid having a polymer concentration of 2.0% and acidic starch concentration of 2.0%. This coating liquid was coated onto medium quality paper having a basis weight of 60 g/m<sup>2</sup> using a gate roll coater followed by drying to obtain a coated paper. The amounts of coated polymer were 0.1 g/m<sup>2</sup> and 0.2 g/m<sup>2</sup>. The results of bursting strength and surface strength tests are shown in Table 3.

[TABLE 3]

Results of Paper Strengthening Effect Test				
No.	Sample Name	Coated Amount (g/m <sup>2</sup> )	Burst Factor	Surface Strength WAX PIC
1	Sample-1	0.1	2.15	12A
2	Sample-1	0.2	2.24	13A
3	Sample-2	0.1	2.14	12A
4	Sample-2	0.2	2.24	13A
5	Acidic starch only	0.6	1.50	11A
6	Non-coated	0.6	1.50	11A

## (EVALUATION)

**[0067]** The paper surface coating liquids prepared from the paper strengthening agents of the present invention can be easily coated onto paper in the form of a diluted dispersion having low viscosity and good workability, and are able to provide paper having high paper strength.

## (SPRAY PAPER STRENGTHENING EFFECT TEST)

**[0068]** Old corrugated cardboard was beaten in a Niagara type beater and adjusted to the freeness of 400 ml of Canadian Standard Freeness (C.S.F.) to prepare pulp. A liquid bond of 2% was added to said pulp followed by stirring to obtain a uniform mixture. The resulting pulp slurry was diluted to 0.5%, and wet paper A was obtained having a dry basis weight of 125 g/m<sup>2</sup> and moisture content of 96% using a hand-made paper tester. Diluted dispersions of each

sample having a polymer concentration of 0.25% were sprayed onto one side of wet paper A using a nozzle at a pressure of 2 atm according to the polymer amounts described in Table 4 (polymer content per solid content of the pulp), followed by suctioning from the opposite side thereof. This a model test in the case of spraying at a wire part for forming paper from pulp slurry. Next, wet paper A was placed between blankets and pressed twice with a test calendar followed by drying to obtain paper for measuring paper strength.

[0069] After adjusting the moisture of the resulting paper for measuring paper strength, bursting strength and ring crush strength were measured, the results of which are shown in Table 4.

[TABLE 4]

Results of Paper Strengthening Effect Test				
No.	Sample Name	Amt. Added (%)	Burst Factor	Ring Crush Strength
1	Sample-1	0.3	2.15	15.02
2	Sample-2	0.3	2.14	15.01
3	Sample-3	0.3	2.14	15.00
4	Sample-4	0.3	2.14	15.01
5	Control-A	0.3	1.89	14.12
6	Control-B	0.3	1.90	14.12
7	Blank	0	1.50	11.73
REMARKS: Control-A is a commercially available mannic paper strengthening agent for wet ends (manufactured by Arakawa Chemical Industries, Ltd., trade name: Polystro 609), while Control-B is a commercially available Hoffman reaction type paper strengthening agent for wet ends (manufactured by Seiko Chemical Industries, Ltd., trade name: Stargum FN). RING CRUSH TEST: TAPPI T472wd-76				

## (EVALUATION)

[0070] The paper strengthening agent of the present invention was able to be sprayed easily in the form of a diluted dispersion with low viscosity and good workability, and paper was able to be provided having good establishment of retention in the paper and high paper strength without the nozzle becoming clogged or the occurrence of non-uniform adhesion.

## (INTERLAYER SEPARATION PREVENTION TEST)

## (EXAMPLE)

[0071] Old corrugated cardboard was beaten in a Niagara type beater and adjusted to the freeness of 400 ml of the Canadian Standard Freeness (C.S.F.) to prepare pulp. A liquid bond of 2% and a commercially available anionic paper strengthening agent of 0.9% were added to the pulp and stirred to mix uniformly. The resulting pulp slurry was diluted to 0.5%, and wet paper A having a dry basis weight of 100 g/m<sup>2</sup> and moisture content of 86% and wet paper B having a dry basis weight of 100 g/m<sup>2</sup> and moisture content of 96% were prepared by a hand-made paper tester. Diluted dispersions of each sample of the present invention having a polymer concentration of 0.5% were sprayed onto one side of wet paper A using a nozzle at a pressure of 2 atm according to the polymer amounts described in Table 5 (polymer content per solid content of the pulp). Thereafter, the coated surface of the wet paper A was overlaid with the surface of wet paper B after which they were placed between blankets and pressed through a test calendar and dried to obtain a dried combination board. After adjusting the moisture of this combination board, the T-peel strength thereof (g/inch) was measured in accordance with J-TAPPI paper pulp test method No. 19-77. The results are shown in Table 5.

## (COMPARATIVE EXAMPLE)

[0072] With the exception of using aqueous polymer solutions by adjusting the diluted dispersions of each sample of the present invention having a polymer concentration of 0.5% used in the examples to pH 7.0 with sodium hydroxide to dissolve the polymer, the same procedure was used as that in the examples. The results are shown in Table 5.



[TABLE 5]

Results of Interlayer Adhesion Effect Test					
	Sample Name	Diluted Dispersion pH	Polymer Added Amount	T-Peel Strength (g/inch)	Spray Form
Example 1	Sample-1	2.7	0.3%	402	Mist
Example 2	Sample-2	2.7	0.3%	400	Mist
Comp. Ex. 1	Sample-1	7.0	0.3%	125	Large drops
Comp. Ex. 2	Sample-2	7.0	0.3%	136	Large drops
Comp. Ex. 3	Sample-3	7.0	0.3%	126	Large drops
Comp. Ex. 4	Sample-4	7.0	0.3%	134	Large drops

**[0073]** The interlayer adhesive paper strengthening agent of the present invention can be easily sprayed in the form of a diluted dispersion having low viscosity and good workability, and combination paper is able to be provided having high interlayer separation effects without the nozzle becoming clogged or the occurrence of non-uniform adhesion.

**[0074]** While the presently preferred embodiments of the present invention have been shown and described, it will be understood that the present invention is not limited thereto, and that various changes and modifications may be made by those skilled in the art without departing from the scope of the invention as set forth in the appended claims.

## Claims

1. A paper strengthening agent comprising a polymer dispersion manufactured by polymerizing a monomer containing (meth)acrylic acid in an aqueous solution and precipitating the produced polymer as fine particles, and which is added to a paper layer after a paper layer is formed, wherein

- (1) the concentration of the (meth)acrylic acid (co)polymer in said polymer dispersion is at least 5 wt%,
- (2) the average particle diameter of the (meth)acrylic acid (co)polymer particles in said polymer dispersion is 1 to 100  $\mu\text{m}$ ,
- (3) the viscosity of said polymer dispersion is 30 to 5000 mPa  $\cdot$  s immediately after and one month after the production,
- (4) the polymer particles can be recognized when said polymer dispersion is diluted 10 times with distilled water and the diluted dispersion is magnified by a factor of 400 and observed with a microscope, and
- (5) when the pH of said diluted dispersion is adjusted to 7.0 by adding an alkali, said polymer particles are dissolved to form an aqueous solution.

2. The paper strengthening agent according to claim 1, wherein said polymer dispersion is polymerized and precipitated in the presence of a dispersibility retaining agent comprising a polyvalent electrolyte.

3. The paper strengthening agent according to claim 1 or claim 2, wherein said dispersibility retaining agent is one selected from a cationic polymer electrolyte, a surface active agent having a polyvalent cationic hydrophilic group and hydrophobic group, and a mixture thereof.

4. The paper strengthening agent according to any one of claims 1 to 3, wherein the weight ratio of the monomer containing (meth)acrylic acid in an aqueous solution to the dispersibility retaining agent is 100:1 to 10:1.

5. The paper strengthening agent according to any one of claims 1 to 4, wherein the viscosity of said polymer dispersion is 30 to 1500 mPa  $\cdot$  s immediately after and one month after the production.

6. The paper strengthening agent according to any one of claims 1 to 5, wherein the dispersibility retaining agent is dimethyldiallylammonium chloride (co)polymer.

7. The paper strengthening agent according to any one of claims 1 to 5, wherein the dispersibility retaining agent is an alkyl group-substituted and/or an aralkyl group-substituted polyethylenepolyamine.

8. The paper strengthening agent according to claim 7, wherein the dispersibility retaining agent is an alkyl group-substituted and/or an aralkyl group-substituted pentaethylenehexamine, the alkyl group having at least 5 carbon atoms.

5 9. A paper strengthening method comprising the steps of: diluting the paper strengthening agent according to any one of claims 1 to 8 with water to prepare a diluted dispersion, coating or impregnating said diluted dispersion onto a dry paper, and drying the treated dry paper.

10 10. A paper strengthening method comprising the steps of: diluting the paper strengthening agent according to any one of claims 1 to 8 with water to prepare a diluted dispersion, and impregnating said diluted dispersion into wet paper on a wire part.

15 11. The paper strengthening method according to claim 10 wherein said diluted dispersion is sprayed to be impregnated into wet paper.

12. The paper strengthening method according to any one of claims 10 and 11, wherein the wet paper treated with said diluted dispersion is of a single layer.

20 13. A paper strengthening method comprising the steps of: diluting the paper strengthening agent according to any one of claims 1 to 8 with water to prepare a diluted dispersion, spraying said diluted dispersion onto a web surface to prepare a plurality of webs having polymer adhered to surfaces thereof, and pressing the surface of said webs so as to be superimposed followed by drying.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 1753

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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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