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PDS

SPECIFICATION

HYM-9701

TITLE OF THE INVENTION

POLYMER DISPERSION, METHOD OF MANUFACTURING
THE SAME, AND USE OF THE SAME

5

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method of manufacturing an anionic polymer dispersion and its use, and
10 more particularly to a method of manufacturing a dispersion of fine particles of (meth)acrylic acid (co)polymer for which curding can be prevented, and also to the use for a low-viscosity dispersion obtained, which can be used with or without diluting with water while omitting a troublesome
15 operation such as neutralization.

2. Background Art

The Laid-Open Japanese Patent Application No. Sho 62-20511 discloses a method of obtaining a water-soluble
20 polymer dispersion by polymerizing monomer in an aqueous salt solution which dissolves the monomer and does not dissolve a formed polymer in the presence of a polymer electrolyte as a dispersant. In this method, the ionic charges of the polymer electrolyte and the used monomers are required to be the same
25 type.

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced



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 which dissolves the monomers but does not dissolve the formed polymer. In this method, the fine particles can be obtained without coexistence 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 technique being different from that proposed in the Laid-open Japanese Patent Application No. Sho 62-20511. However, the fine particles in the dispersion of acrylic polymer-acrylamide copolymer by said method has a property of being agglomerated by keep standing and is solidified and curded to a bean curd shape, thereby making this method not practical at all. Because of this, the industrial application of said dispersion became impossible.

SUMMARY OF THE INVENTION

The general object of the present invention is to provide a method of manufacturing a dispersion of the fine particles of (meth)acrylic acid (co)polymer for which the curding can be prevented and also to provide the use of a low-viscosity dispersion which can be used with or without diluting with water while omitting a troublesome process such

as neutralization or the like.

The inventors of the present invention discovered that a dispersion of fine polymer particles having a low viscosity, good workability and excellent stability for
5 preservation can be manufactured by polymerizing water-soluble monomer(s) comprising (meth)acrylic acid in an aqueous salt solution, which dissolves said monomer(s) and does not dissolve formed polymer in the presence of polymer electrolyte as a dispersibility retaining agent, and then the
10 inventors contrived the present invention.

An object of the present invention is to provide a method of manufacturing a polymer dispersion of a (meth)acrylic acid (co)polymer by polymerizing a water-soluble monomer(s) comprising (meth)acrylic acid in an
15 aqueous salt solution in the presence of a dispersibility retaining agent comprising a polymer electrolyte soluble in said aqueous salt solution, wherein

- (1) the concentration of the (meth)acrylic acid (co)polymer in said polymer dispersion is at least 5 wt%,
- 20 (2) the average particle diameter of the (meth)acrylic acid (co)polymer particles in said polymer dispersion is 1 to 100 μm ,
- (3) the viscosity of said polymer dispersion is 10 to 3000 cp immediately after and one month after the production,
- 25 (4) the polymer particles can be recognized when said



polymer dispersion is diluted 10 times with distilled water and the diluted solution is enlarged and observed 400 times with a microscope, and

(5) when the pH of said diluted solution of the
5 dispersion is adjusted to 7.0 by adding alkali, said polymer particles are dissolved to form an aqueous solution.

Another object of the present invention is to provide a method of manufacturing a polymer dispersion having the composition of a water-soluble monomer(s) which is(are)
10 to be polymerized and comprise(s) (meth)acrylic acid, which is 15 to 100 mol% of (meth)acrylic acid and 0 to 85 mol% of acrylamide in said manufacturing method.

A further object of present invention is to provide a method of manufacturing a polymer dispersion, wherein the
15 dispersibility retaining agent is selected from the group consisting of dimethyldiallylammonium chloride (co)polymer, acrylamide-2-methylpropane sulfonic acid (co)polymer, and a mixture thereof in said manufacturing method.

Also another object is to provide a method for
20 manufacturing a polymer dispersion wherein a weight ratio of the water-soluble monomer(s) which is(are) to be polymerized and comprise(s) (meth)acrylic acid to the dispersibility retaining agent is 100:1 to 10: 1 in said manufacturing method.

25 A further object of the present invention is to



provide a (meth)acrylic acid (co)polymer dispersion in aqueous salt solution, wherein

- (1) the concentration of the (meth)acrylic acid (co)polymer in said polymer dispersion is at least 5 wt%,
- 5 (2) the average particle diameter of (meth)acrylic acid (co)polymer particles in said polymer dispersion is 1 to 100 μm ,
- (3) the viscosity of said polymer dispersion is 10 to 3000 cp immediately after and one month after the production,
- 10 (4) the polymer particles can be recognized when said polymer dispersion is diluted 10 times with distilled water and the diluted solution is enlarged and observed 400 times with a microscope, and
- (5) when the pH of said diluted solution of said
- 15 dispersion is adjusted to 7.0 by adding alkali, said polymer particles are dissolved to form an aqueous solution.

A further object of the present invention is to provide a papermaking method comprising dispersing cellulose pulp and fillers in water to prepare a pulp slurry while

20 maintaining the pH of the slurry in the range of 6.5 to 10, forming a sheet, and drying it to make a paper, said method further comprising adding a cationic polymer into said pulp slurry, shearing said pulp slurry, and adding said polymer dispersion diluted with water before forming said sheet.

25 Also another object of the present invention is to



provide a method for improving soil containing moisture comprising adding and mixing said polymer dispersion of 0.1 to 5 kg as polymer content per 1 m³ of said soil having a water content of 20 to 400% thereby preparing soils with
5 filling-in possible.

Also a further object is to provide a method of preventing interlayer peeling-off comprising spraying said polymer dispersion diluted with water as an interlayer peeling-off prevention agent to the surfaces of web,
10 overlaying the surfaces of a plurality of webs with the interlayer peeling-off prevention agent stuck on the surfaces, and then pressing and drying the layers.

Also another object of the present invention is to provide a method of flocculating a solid suspension,
15 comprising adding and mixing said polymer-dispersion to the solid suspension in a state of no dilution or a state of dispersion diluted with water.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 In the present invention the monomer(s) which is(are) to be polymerized and comprise(s) (meth)acrylic acid includes 15 to 100 mol% of monomer(s) selected from the group consisting of acrylic acid, methacrylic acid and a mixture thereof, and 0 to 85 mol% of nonionic monomer(s) selected
25 from the group consisting of acrylamide, acrylonitrile,

methyl(meth)acrylate, hydroxyethyl(meth)acrylate,
vinylmethylether, vinylacetate and a mixture thereof.

Among them, a copolymer of (meth)acrylic acid and
acrylamide is most preferable. Further, a ternary copolymer
5 further containing acrylonitrile can be used desirably.

The dispersibility retaining agent used in the
present invention is a polymer electrolyte having the role of
retaining the dispersibility after the formation of a
dispersion. The polymer electrolyte may be a cationic one or
10 an anionic one.

Examples of the cationic polymer electrolyte as the
dispersibility retaining agent used in the present invention
are (co)polymers of salts or quaternary products of
dialkylaminoalkyl(meth)acrylate, (co)polymers of salts or
15 quaternary products of dialkylaminoalkyl(meth)acrylamide, and
(co)polymers of dialkyldiallylammonium salt.

Examples of the salts or quaternary products of
dialkylaminoalkyl(meth)acrylate are
dimethylaminoethyl(meth)acrylate hydrochloride,
20 acryloyloxyethyltrimethylammonium chloride and the like.
Also, examples of the salts or quaternary products of the
dialkylaminoalkyl(meth)acrylamide are hydrochlorides or
methylated products of dimethylaminopropyl(meth)acrylamide.
An example of dialkyldiallylammonium salt is
25 dimethyldiallylammonium chloride.



Also, examples of the anionic water-soluble polymer electrolyte are (co)polymers obtained by polymerizing monomers selected from the group consisting of styrene sulfonic acid or a salt thereof, vinyl sulfonic acid or a salt thereof, acrylamide-2-methylpropane sulfonic acid or a salt thereof, and the like.

The polymer electrolyte stated above can be a copolymer having at least one kind of ionic monomers or can be a copolymer further with nonionic monomers such as acrylamide.

The most preferable cationic polymer electrolyte as the dispersibility retaining agent for the present invention is a (co)polymer of dimethyldiallylammonium chloride, and the most preferable anionic polymer electrolyte is a (co)polymer of acrylamide-2-methylpropane sulfonic acid.

The weight ratio of the monomer(s) which is(are) to be polymerized and comprise(s) (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 is curded with time to a bean curd shape. On the other hand, if it is excessive, the effect thereof is limited to be economically meaningless.

Examples of the salt forming the aqueous salt solution used for the present invention are alkaline metal salts such as sodium salt, potassium salt and the like, and



ammonium salt such as ammonium chloride, ammonium sulfate, ammonium nitrate and the like. The concentration of the salt used in the aqueous salt solution of the above is from 5 wt% to saturated concentration as required, but it is required
5 that the concentration of the salt and the pH of the dispersion be in a range where the aqueous salt solution dissolves the used monomers but does not dissolve the formed polymer. On the other hand, the coexisting dispersibility retaining agent comprising a polymer electrolyte must be
10 soluble in said aqueous salt solution.

The (meth)acrylic acid (co)polymer dispersion and the polymer electrolyte as a dispersibility retaining agent in the present invention can respectively be prepared by dissolving monomer(s) in an aqueous medium under nitrogen
15 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) chloride or a water-soluble redox type polymerization initiator using both ammonium persulfate and sodium hydrogen sulfite.

20 Temperature of the polymerization system can be selected arbitrarily depending on the property of the used polymerization initiator from the range of 0 to 100°C. For adjusting the molecular weight of the obtained polymer, a chain transfer agent such as isopropylalcohol or mercaptan
25 can be added and used by arbitrary selection as same as



ordinary radical polymerization. At the time of preparing (meth)acrylic acid (co)polymer dispersion, stirring with a peripheral speed of more than 1 m/min must be performed for smoothening the deposition of fine polymer particles. Unless
5 the content overflows from the equipment, there is no upper limit of the stirring speed and any stirring conditions can be selected. The polymer electrolyte as a dispersibility retaining agent is generally performed by the stationary polymerization in an aqueous solution, but the polymerization
10 therefor in the present invention is preferably performed under stirring from the viewpoint of the homogenization of products.

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

The dispersion of the present invention contains a high concentration of formed polymer but the viscosity of the dispersion is low because the polymer is stably dispersed in a dispersion medium in a state of fine particles and thus the
20 viscosity thereof is normally low or 10 to 3000 cp.

Therefore, as its characteristics, the polymer dispersion can flow easily and can be handled very easily.

The polymer particles in the dispersion of the present invention can be recognized in a non-diluted state
25 and in a state diluted 10 times with distilled water when it



is enlarged 400 times by an optical microscope. At this time, the average particle diameter of the polymer particles is normally 1 to 100 μm and is preferably 2 to 30 μm , and more preferably 2 to 20 μm . When the average particle
5 diameter of the polymer particles exceeds 100 μm , the particles tend to be deposited easily and thus settling stability is degraded and a long time becomes necessary for complete dissolving the polymer when used. On the contrary, the dispersion of the present invention has excellent
10 settling stability and any trouble such as sticking of particles each other thereby creating masses will never occur even from storage at the normal temperature. And also the solubility thereof to water during the use is very excellent.

The molecular weight of the polymer in the
15 dispersion of the present invention is not specially limited. A larger molecular weight is more preferable when considering the use as chemicals to be added for flocculating and treating sludge, chemicals to be added for flocculating and dewatering, and chemicals to be used for paper making
20 processes. In this case, desired molecular weight is more than 1 million. 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 Brookfield viscometer) in such a
25 manner that the concentration of the polymer becomes 0.5 wt%,

it is normally in the range of 5 to 200 cp. Also, the dispersion of the present invention hardly has any change in viscosity with time even after the storage for 1 month.

When the dispersion of the present invention is
5 diluted 10 times, the polymer particles can be recognized with a microscope and when an alkali is added to the solution 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 as a
10 dispersion of the fine particles of water-insoluble polymer.

In the papermaking method using the dispersion of the present invention, cationic polymer such as an aqueous solution of cation starch or cationic polyacrylamide is added
15 to and mixed together with a pulp slurry the pH of which is adjusted to the range of 6.5 to 10 after dispersing cellulose pulp and filler in water, and shearing force is applied, and thereafter the polymer dispersion diluted with water of the present invention is added. That is, the present invention
20 is characterized in that the polymer comprising a monomer containing (meth)acrylate is not used. The (meth)acrylic acid (co)polymer is hard to dissolve and has a low viscosity even though the molecular weight is high, and vigorous agitation is not required for dispersing and mixing this
25 polymer into paper materials.

At this time, the amount of the cationic polymer added is preferably 0.1 to 2 wt% per paper material SS. When using cation starch, the ratio of cationization thereof is preferably 1 to 7 mol%.

5 The pulp slurry used in the present invention has pH 6.5 to 10 and thus this is for neutral paper making. In that pH range, (meth)acrylic acid (co)polymer is dissociated to (meth)acrylate (co)polymer, a cohesion is created by the synergetic effect with the cationic polymer added in the
10 previous stage with increased viscosity, and retention and freeness can be improved.

Amount of (meth)acrylic acid (co)polymer added which is effective for improving the retention and freeness is 0.002 to 0.05 wt% per paper material SS, and more
15 preferably 0.005 to 0.02 wt%. If the added amount is too little, there will be no effect of improving the retention and freeness; if too excessive, flocking texture occurs and the quality of the paper produced is worsened.

20 When using the polymer dispersion of the present invention as a soil improvement agent for soil containing water, normally the polymer dispersion as a raw material is used as it is without dilution; that is, 0.1 to 5 kg of polymer content is mixed per 1 m³ soil containing 20 to 400%
25 of water ratio and soil with filling-in possible can be

prepared. If necessary, a proper amount of cement and/or lime can be added and mixed. For the lime, slaked lime or quick lime may be used. In this case, the weight ratio of the polymer content of polymer dispersion to cement and/or
5 lime is desired to be 1:1 to 1:500. In the present invention, the polymer dispersion to be added can be more easily added and mixed compared to conventional powdered one, and contamination by oil or generation of odor like emulsion is not accompanied as some of advantages of this invention.

10

In the interlayer peeling-off prevention method according to the present invention, the polymer dispersion of the present invention diluted with water as an interlayer peeling-off prevention agent is stuck to the surfaces of webs
15 by spraying; a plurality of webs stuck with the interlayer peeling-off prevention agent on the surfaces are pressed in such a manner that said surfaces are overlapped each other and then dried. At this time, the polymer dispersion diluted with water should have a pH of no more than 4.0, and
20 preferably no more than pH 3.5, and thereby most of (meth)acrylic acid group are not dissociated. The polymer concentration in the solution diluted with water is preferably 0.1 to 1.5 wt%, and the viscosity thereof is preferably 1 to 50 cp. The amount of the polymer stuck is
25 preferably 0.1 to 1.5 wt% per pulp solid content. Also in

the method of the present invention, the conventional interlayer peeling-off prevention agents such as starch, modified starch, casein, galactomannan, etc. may be used together.

5 In the method of the present invention, there is no possibility of decay such as conventional interlayer peeling-off prevention agent such as starch, and also there is no worry of the difficult spraying as a result of increased viscosity.

10

 In the flocculating method of the present invention, the polymer dispersion of the present invention is added and mixed as a high molecular flocculant in a state of no dilution or a state of dilution with water to solid
15 suspension. At this time, the polymer dispersion or the solution diluted with water is preferably no more than pH 4.0, more preferably no more than 3.5. In the method of the present invention, addition of flocculant only by direct or simple dilution is possible as a merit, and troublesome
20 dissolving operation can be omitted.

EXAMPLES

(PREPARATIVE EXAMPLE - 1)

 In a reactor equipped with a stirrer, a nitrogen
25 aeration pipe and a temperature controller, 79 parts of 20

wt% sodium chloride aqueous solution was placed, and 20 parts of monomers having the composition of 35 mol% of acrylic acid and 65 mol% of acrylamide, and 1 part of polydimethyldiallylammonium chloride as a dispersibility
5 retaining agent (manufactured by CPS Co., trade name: Age Flock WT40HV) were dissolved therein. Thereafter, as a polymerization initiator, 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added by 500 ppm against monomer. Under stirring, the polymerization was
10 carried out for 10 hours at 53°C, and a polymer dispersion (pH 3) with 10 to 20 µm fine particles dispersed in the aqueous salt solution was obtained. This dispersion was named as "Sample-1". Viscosity of said polymer dispersion was no more than 500 cp, fine particles were recognized with
15 a microscope after diluting 20 times with deionized water, and the polymer was essentially recognized to be water-insoluble. Sodium carbonate aqueous solution was mixed in said dispersion to adjust the pH of the dispersion to 7, then the polymer was dissolved and the molecular weight
20 thereof was determined from the intrinsic viscosity based on said aqueous solution.

(PREPARATIVE EXAMPLE - 2)

The same operation as that of the preparative
25 example-1 was performed except using monomers of 55 mol% of

acrylic acid and 45 mol% of acrylamide, and thereby a water-insoluble polymer dispersion was obtained. This dispersion was named as "Sample-2".

5 (PREPARATIVE EXAMPLE - 3)

The same operation as that of the preparative example-1 was performed except using monomers of 90 mol% of acrylic acid and 10 mol% of acrylamide, and thereby a water-insoluble polymer dispersion was obtained. This
10 dispersion was named as "sample-3".

(PREPARATIVE EXAMPLE - 4)

The same operation as that of the preparative example-1 was performed except using a homopolymer of
15 acrylamide-2-methylpropane sulfonic acid soda (intrinsic viscosity of 1 dl/g) as a dispersibility retaining agent, and thereby a water-insoluble polymer dispersion was obtained. This dispersion was named as "Sample-4".

20 (COMPARATIVE PREPARATIVE EXAMPLE-1)

The same operation as that of the preparative example-1 was performed except not using any dispersibility retaining agent and thereby a water-insoluble polymer dispersion was obtained. This dispersion was named as
25 "Comparative Sample-1". The Comparative Sample-1 began to

lose its fluidity after 1 hour of stationary state,
solidified to bean curd shape 5 hour later, thereby causing
curding and unusable condition. Therefore, the Comparative
Sample-1 cannot be called as a dispersion.

5

(COMPARATIVE PREPARATIVE EXAMPLE-2)

The same operation as that of the preparative
example-2 was performed except not using any dispersibility
retaining agent, and thereby a water-insoluble polymer
10 dispersion was obtained. This dispersion was named as
"Comparative Sample-2". The Comparative Sample-2 began to
lose its fluidity after 1 hour of stationary state,
solidified to bean curd shape 5 hour later, thereby causing
curding and unusable condition. Therefore, the Comparative
15 Sample-2 cannot be called as a dispersion

(COMPARATIVE PREPARATIVE EXAMPLE-3)

The same operation as that of the preparative
example-3 was performed except not using any dispersibility
20 retaining agent, and thereby a water-insoluble polymer
dispersion was obtained. This dispersion was named as
"Comparative Sample-3". The Comparative Sample-3 began to
lose its fluidity after 1 hour of stationary state,
solidified to bean curd shape 5 hour later, thereby causing
25 curding and unusable condition. Therefore, the Comparative

Sample-3 cannot be called as a dispersion.

(COMPARATIVE PREPARATIVE EXAMPLE-4)

80 parts of deionized water and 20 parts of
5 monomers having the composition of 35 mol% of sodium acrylate
and 65 mol% of acrylamide were placed in a reactor coated
with Teflon. After nitrogen aeration, 1% aqueous solution of
2,2'-azobis(2-amidinopropane) hydrochloride was added as a
polymerization initiator with 100 ppm against monomer. The
10 polymerization was performed for 10 hours in a stationary
state at 48°C and a polymer in a gel state was obtained. The
gel obtained was roughened with an extruder, dried with a
ventilating dryer and crushed into fine powder with a
crusher. These fine particles of the water-soluble polymer
15 were called as "Comparative Sample-4".

Polymer characteristics of the Sample-1 to
Comparative Sample-4 are shown in Table 1.

[TABLE 1]

No.	Sample Name	Ratio of Monomer Composition (mol%)			Kind of Dispersibility Retaining Agent	Molecular Weight (millions)	Properties one day later
		NaAAc	HAAC	AAM			
1	Sample-1	0	35	65	PDDAC	4.5	O
2	Sample-2	0	55	45	PDDAC	4.5	O
3	Sample-3	0	90	10	PDDAC	4.5	O
4	Sample-4	0	35	65	PAMPS	4.5	O
5	Comparative Sample-1	0	35	65	-	4.5	X
6	Comparative Sample-2	0	55	45	-	4.5	X
7	Comparative Sample-3	0	90	10	-	4.5	X
8	Comparative Sample-4	35	0	65	-	4.5	□

NaAAc: Sodium acrylate

HAAC: Acrylic acid

AAM: Acrylamide

PDDAC: Polydimethyldiallylammonium chloride

PAMPS: Polyacrylamide-2-methylpropane sulfonic acid soda

O: Good fluidity

x: Curding

□: Fine powder

(SYNTHESIS OF CATION STARCH)

The raw material starch described in Table 2 was prepared with 3-chloro-2-hydroxypropyltrimethylammonium chloride as a starch cationizing agent (manufactured by Mollin Chemical Co., trade name: COPA-60S) under an alkali

condition by sodium hydroxide, and cation starches to be used in the examples were obtained. Compositions of each of the cation starches are shown in Table 2.

5 [TABLE 2]

No.	Sample Name	Percentage of Cationization	Raw Material
1	CS-1	5 mol%	Tapioca Starch
2	CS-2	2 mol%	Tapioca Starch
3	CS-3	5 mol%	Corn Starch
4	CS-4	2 mol%	Corn Starch

(PAPERMAKING TEST-1)

Filler retention and total retention were measured with a britt type dynamic jar tester and the results are shown in Table 3. Paper materials used for the test were 900 ppm of calcium carbonate, 300 ppm of kaolin, 4000 ppm of pulp, pH 8.1, and CSF of 300 ml for medium quality paper. In the test procedure, 500 ml of paper materials were put in the britt type dynamic jar tester, agitation was started at 1,500 rpm, an aqueous solution of 0.1 wt% of cationic starch described in Table 2 was added. 30 seconds later, a 0.1 wt% aqueous solution diluted with water of the polymer dispersion described in Table 1 was added. Further, 30 seconds later, a cock for sampling white water was opened, and white water passed 150 mesh wires was flowed out. White water in an

early stage of 10 seconds was discarded, and white water for 30 seconds thereafter was sampled and subjected to the measurement. The total retention and the filler retention by ashing at 600°C were determined. Amounts of chemicals added are the amount added per SS portion of paper material.

[TABLE 3]

	Cation Starch		Acrylic Acid (Co)Polymer		Filler Retention (%)	Total Retention (%)
	Sample Name	Amount Added (ppm)	Sample Name	Amount Added (ppm)		
Example 1	CS-1	10000	Sample-1	250	64.0	85.0
Example 2	CS-2	10000	Sample-2	250	64.0	85.0
Example 3	CS-3	10000	Sample-3	250	64.0	85.0
Example 4	CS-4	10000	Sample-4	250	63.5	83.0
Example 5	CS-1	3000	Sample-1	250	59.5	76.0
Comparative Example 1	CS-1	10000	Not added	0	45.5	67.5
Comparative Example 2	CS-2	10000	Not added	0	42.5	67.2
Comparative Example 3	CS-3	10000	Not added	0	43.5	67.0

(PAPERMAKING TEST-2)

Filler retention and total retention were measured with a britt type dynamic jar tester, and the results are shown in Table 4. Paper material subjected to the tests was medium quality paper with 900 ppm of calcium carbonate, 300 ppm of kaolin, 4,000 ppm of pulp, pH 8.1, and CSF of 300 ml.

In the test procedure, 500 ml of the paper materials were put in the britt type dynamic jar tester, agitation was started at 1,500 rpm, a 0.1 wt% aqueous solution of copolymer of acrylamide-acryloyloxyethyltrimethylammonium chloride

5 (manufactured by HYMO CO., trade name: HYMOLOC NR12ML) was added. Further 30 seconds later, a cock for sampling white water was opened, and white water passed 150 mesh wires was flowed out. White water in an early stage of 10 seconds was discarded, white water for 30 seconds thereafter was sampled
10 and measured. The total retention and the filler retention by ashing at 600°C were determined. Amounts of chemicals added were the amount added per SS portion of paper materials, and HYMOLOC NR12ML was called as a prestage polymer, and the polymer shown in Table 1 was called as a
15 poststage polymer.

[TABLE 4]

	Prestage Polymer	Poststage Polymer		Filler Retention (%)	Total Retention (%)
	Amount Added (ppm)	Sample Name	Amount Added (ppm)		
Example 6	250	Sample-1	150	64.5	85.0
Example 7	250	Sample-2	150	64.6	85.0
Example 8	250	Sample-3	150	64.5	85.0
Example 9	250	Sample-4	150	64.0	84.5
Comparative Example 4	250	Not added	0	43.5	67.0
Comparative Example 5	300	Not added	0	44.5	67.7
Comparative Example 6	350	Not added	0	45.5	68.2

[EVALUATION]

By the papermaking method of the present invention, the retention of cellulose fibers and fillers can be improved in papermaking process. Said object can be achieved by using
5 acrylic acid (co)polymer of a high molecular weight effective for flocculation under good working condition with low viscosity, and this creates a high economic effect.

(TEST FOR SOIL CONTAINING WATER)

10 Clayey soil having a water content of 156% was put from one end of a mixer equipped with a biaxial puddle, each sample and quick lime were successively added from a pump or a feeder and mixed and discharged from other end for improving the soil. Amounts of chemicals added are shown in
15 Table 5 in Kg number per 1 m³ of soil containing water. As a test sample, part of improved soil was sampled, the shape of the improved soil was confirmed by visual observation and the soil was tightly sealed for preventing the scattering of moisture and then cured for 6 days. Said improved soil was
20 subjected to tamping test in accordance with JIS A 1210 (Tamping test method by tamping) by placing the improved soil in three layers in a mold having an inner diameter of 15 cm and by tamping each layer respectively 92 times with a 4.5 Kg rammer. Next, preparation for water immersion and expansion
25 test was made in accordance with JIS A 1211 (CBR test

method), and soil was immersed in a water tank for 4 days and the amount of expansion was pursued. Amounts of water immersion and expansion in the samples of the preferred embodiment of the present invention were all no more than 1%.

5 Moreover, water taken out from the water tank was removed, predetermined measurements were made 15 minutes later, a load-penetration curves were determined by a CBR tester, and a load at the penetration of 2.5 mm, that is, penetration strength was measured. The results of the test
10 are shown in Table 5.

[TABLE 5]

	Polymer		Amount of Quick Lime Added (Kg/m ³)	Penetration Intensity (Kg)	State of Improved Soil
	Sample Name	Amount Added (Kg/m ³)			
Example 10	Sample-1	1.4	0	27.3	O
Example 11	Sample-2	0.7	50	57.2	O
Example 12	Sample-3	0.7	50	55.4	O
Example 13	Sample-4	0.7	50	56.7	O
Comparative Example 7	Comparative Sample-4	0.7	50	-	X
Comparative Example 8	Comparative Sample-4	1.4	50	-	X

O: Granular with rustling sound

X: Soft and impossible for mixing

[EVALUATION]

By the method of the present invention for

improving soil containing much water, the improved soil has a low viscosity and excellent kneading property, can be easily mixed with a machine, is granular and has a rustling sound, can be reused for filling-in, prevents environmental
5 destruction, thereby greatly contributing to the communities.

(INTERLAYER PEELING-OFF PREVENTION TEST)

Old corrugated cardboard was beaten in a Niagara type beater and adjusted to the freeness of 400 ml of the
10 Canadian Standards, and pulp was prepared. A liquid bond of 2% was added to said pulp, an anionic paper strengthening agent available on the market was added by 0.9% to the pulp and agitated and mixed uniformly. Pulp slurry obtained was diluted up to 0.5%; a wet paper A having a moisture content
15 of 86% and a wet paper B having a moisture content of 96% per dry weighed amount of 100 g/m² were prepared by a hand-made paper tester. A diluted solution of an interlayer peeling-off prevention agent with a polymer concentration of 0.5% with the polymer amount shown in Table 6 (polymer content per
20 solid content of the pulp) was sprayed from a nozzle under 2 atmospheric pressure to the one surface of the wet paper A. Thereafter, the coated surface of the wet paper A was overlaid with the surface of wet paper B; they were placed between blankets and pressed through a test calendar and
25 dried, and a dried combination board was obtained. Moisture

of this combination board was adjusted and the T-peel strength thereof (g/inch) were measured in accordance with J-TAPPI paper pulp test method No.19-77. The results are shown in Table 6.

5

(COMPARATIVE EXAMPLES OF INTERLAYER PEELING-OFF PREVENTION TEST)

A solution diluted with water of the interlayer peeling-off prevention agent with 0.5% polymer concentration used in the application example was adjusted to pH 7.0 with sodium hydroxide and used as an aqueous polymer solution and, otherwise, operation as same as the above was carried out. The results are shown in Table 6.

[TABLE 6]

	Polymer		pH of Solution Diluted With Water	T-peel Strength (g/inch)	Shape of Spray
	Sample Name	Amount Added (%)			
Example 14	Sample-1	0.3	2.7	402	Mist
Example 15	Sample-2	0.3	2.7	400	Mist
Example 16	Sample-3	0.3	2.7	398	Mist
Example 17	Sample-4	0.3	2.7	400	Mist
Comparative Example 9	Sample-1	0.3	7.0	125	Large Drops
Comparative Example 10	Sample-2	0.3	7.0	136	Large Drops
Comparative Example 11	Sample-3	0.3	7.0	126	Large Drops
Comparative Example 12	Sample-4	0.3	7.0	134	Large Drops

[EVALUATION]

According to the interlayer peeling-off prevention method of the present invention, said solution with diluted water having a low viscosity and good workability can be easily sprayed without clogging of spray nozzle or non-uniform sticking due to difficulty in spraying, thereby providing combination board having a high interlayer peeling-off prevention effect.

10 (FLOCCULATION TEST 1)

In a flocculation and agitation tank, water 10 times the volume of the raw solution of the dispersion was supplied under pressure to the deliver side of an accurate volume pump to muddy water as waste water from washing aggregates of concrete work while supplying the raw solution as sample-1 with the accurate volume pump to perform dilution with water within 1 second of residence time in the piping. Flocculation treatment was performed by mixing and agitation. Settling and separation were performed with a thickener and good settlement was achieved.

In the same manner, flocculation treatment was performed by a solution diluted 10 times using the raw material of the Sample-4 and the settlement was very good. Compared to this, the Comparative Sample-1 had no fluidity, and the supplying of raw solution by the accurate volume pump

was impossible.

(FLOCCULATION TEST 2)

In a flocculation treatment where bauxite was
5 treated by caustic soda and impurities (normally called red
mud) in a solution where sodium aluminate was dissolved were
flocculated and settled, the Sample-3 as a raw material was
added and supplied with an accurate volume pump to a
flocculation and agitation tank and treatment was carried
10 out. Thereafter, solid-liquid separation was performed in a
clarifier and good separation performance was recognized.
Compared to this, the Comparative Sample-3 had no fluidity,
and the supplying of raw solution by an accurate volume pump
was not possible.

15

[EVALUATION]

In the flocculation method for the solid by the
present invention, large-scale dissolving facilities required
for ordinary powdered high polymer flocculant are
20 unnecessary. Also, there is no possibility to bring an oil,
which is a water pollutant, to the system when using
water-in-oil type high polymer flocculant. A polymer
flocculant dispersion manufactured by jointly using a
dispersibility retaining agent together according to the
25 present invention is stable for a long period of time and

thus the raw material, for example, can be supplied as it is
by an accurate volume pump. Economic value of the product
obtained from the present invention is therefore high in view
of the cost merit of the facility phase as well as the
5 workability.

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,
10 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.



WHAT IS CLAIMED IS:

1. A method of manufacturing a polymer dispersion of (meth)acrylic acid (co)polymer by polymerizing a water-soluble monomer(s) comprising (meth)acrylic acid in an aqueous salt solution in the presence of a dispersibility retaining agent comprising a polymer electrolyte soluble in said aqueous salt solution, wherein
 - (1) the concentration of the (meth)acrylic acid (co)polymer in said polymer dispersion is at least 5 wt%,
 - 10 (2) the average particle diameter of (meth)acrylic acid (co)polymer particles in said polymer dispersion is 1 to 100 μm ,
 - (3) the viscosity of said polymer dispersion is 10 to 3000 cp immediately after and one month after the production,
 - 15 (4) the polymer particles can be recognized when said polymer dispersion is diluted 10 times with distilled water and the diluted solution is enlarged and observed 400 times with a microscope, and
 - (5) when the pH of said diluted solution of said
 - 20 dispersion is adjusted to 7.0 by adding alkali, said polymer particles are dissolved to form an aqueous solution.
2. The method of manufacturing a polymer dispersion according to claim 1, wherein the composition of the
- 25 water-soluble monomer(s) which is(are) to be polymerized and

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED



comprise(s) (meth)acrylic acid is(are) 15 to 100 mol% of acrylic acid and 0 to 85 mol% of acrylamide.

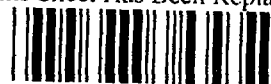
3. The method of manufacturing a polymer dispersion according to claim 1 or 2, wherein the dispersibility retaining agent is selected from the group consisting of dimethyldiallylammonium chloride (co)polymer, acrylamide-2-methylpropane sulfonic acid (co)polymer, and a mixture thereof.

10

4. The method for manufacturing a polymer dispersion according to claim 1 or 2, wherein the weight ratio of the water-soluble monomer(s) which is(are) to be polymerized and comprise(s) (meth)acrylic acid to the dispersibility retaining agent is 100:1 to 10:1.

5. The method of manufacturing a polymer dispersion according to claim 3, wherein the weight ratio of the water-soluble monomer(s) which is(are) to be polymerized and comprise(s) (meth)acrylic acid to the dispersibility retaining agent is 100:1 to 10:1.

6. A (meth)acrylic acid (co)polymer dispersion in an aqueous salt solution, wherein
25 (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 μm ,

5 (3) the viscosity of said polymer dispersion is 10 to 3000 cp 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 solution is enlarged and observed 400 times
10 with a microscope, and

(5) when the pH of said diluted solution of said dispersion is adjusted to 7.0 by adding alkali, said polymer particles are dissolved to form an aqueous solution.

15 7. A method of papermaking, comprising dispersing cellulose pulp and fillers in water to prepare a pulp slurry while maintaining the pH of the slurry in the range of 6.5 to 10, forming a sheet from the pulp slurry and drying it to make a paper, said method further comprising adding a
20 cationic polymer to said pulp slurry, shearing said pulp slurry and thereafter adding the polymer dispersion according to claim 6 diluted with water before forming the sheet.

8. The method of papermaking according to claim 7,
25 wherein the cationic polymer is selected from the group



consisting of cation starch, cationic polyacrylamide, and a mixture thereof.

9. A method for improving soil containing moisture,
5 comprising mixing the polymer dispersion according to claim 6
of 0.1 to 5 kg as polymer content per 1 m³ of said soil
having a water content of 20 to 400% to prepare soils with
filling-in possible.
- 10 10. A method of preventing interlayer peeling-off,
comprising spraying the polymer-dispersion according to claim
6 diluted with water as an interlayer peeling-off prevention
agent to the surfaces of web, overlaying the surfaces of a
plurality of webs with the interlayer peeling-off prevention
15 agent stuck on the surfaces, and then pressing and drying the
layers.
11. A method of flocculating a solid suspension,
comprising adding and mixing the polymer dispersion according
20 to claim 6 to a solid suspension in a state of no dilution or
in a state of dispersion diluted with water.