

SPECIFICATION

METHOD FOR PRODUCING AQUEOUS ACRYLIC ACID POLYMER SOLUTION

[TECHNICAL FIELD]

[0001]

The present invention relates to a method for producing an aqueous solution including an acrylic acid-based polymer that is suitable as an inorganic particle dispersant, a water treatment agent, and the like.

[BACKGROUND ART]

[0002]

It is known that an acrylic acid-based polymer having a structural unit derived from acrylic acid or a salt thereof, is suitable as an inorganic particle dispersant; a scale inhibitor that is used for a pipe, a boiler, a heat exchanger, and the like; a detergent builder; and the like. It is considered that an acrylic acid-based polymer that mainly includes a low-molecular-weight polymer (i.e., a polymer having a weight average molecular weight (Mw) of 2,000 to 10,000, and has a dispersity (molecular weight distribution) (Mw/Mn) (that is calculated by dividing the weight average molecular weight (Mw) by the number average molecular weight (Mn)) as small (narrow) as possible) is suitable for these applications.

It is desirable to use an efficient production method that can achieve a reduction in reaction time, an improvement in productivity, and the like when producing such a polymer. A continuous production method is being developed as such a production method in addition to a batchwise production method.

[0003]

The following technique is known as a method for continuously producing an acrylic acid-based low-molecular-weight polymer.

Patent Document 1 discloses a method for continuously producing a polyacrylate aqueous solution having a pH of 6 to 9, wherein an acrylic acid monomer, or an acrylic-based monomer mainly including an acrylate monomer, is polymerized in an aqueous medium to continuously produce a polyacrylate, the method being characterized in that a continuous reaction device including a plurality of reactors is used, wherein at least the first reactor is a tank-type reactor, the monomer is polymerized in the aqueous medium of which the pH is maintained to be 3.5 or less while continuously charging the first reactor with an acrylic-based monomer, an initiator, and hydrogen sulfite, a reaction liquid discharged from the first reactor is continuously fed to the second reactor, and polymerization is effected in the second reactor while an alkali is added to the reaction liquid in the second reactor, the third reactor, or the subsequent reactor to effect neutralization.

Patent Document 2 discloses a method for continuously producing a water-soluble acrylic-based polymer, wherein an acrylic acid monomer, or an acrylic-based monomer mainly including an acrylate

monomer, is polymerized in an aqueous medium, and an alkali is, if necessary, added to the mixture to continuously produce a water-soluble acrylic-based polymer, the method being characterized in that a continuous reaction device having a plurality of reactors is used, wherein at least the first reactor is a tank-type reactor, the acrylic-based monomer is polymerized while continuously charging the first reactor with the acrylic-based monomer, an initiator, and a chain transfer agent, and the polymerization conversion rate of the monomer fed to the first reactor is maintained to be 90% or more by mass with respect to the reaction liquid discharged from the first reactor.

Patent Document 3 discloses a method for continuously producing a water-soluble polymer (polyacrylic acid (salt)) having a step that circulates a circulating liquid including a monomer (acrylic acid) having a polymerizable unsaturated bond through a reactor that has a circulation line including a tank and a circulation pipe provided outside the tank, to continuously produce a water-soluble polymer, and a step that removes part of the circulating liquid from a discharge line, wherein a cooler is provided to the circulation line at at least one position.

[PRIOR TECHNICAL DOCUMENT]

[PATENT DOCUMENT]

[0004]

[Patent Document 1] JP-A 2003-2909

[Patent Document 2] JP-A 2003-40912

[Patent Document 3] JP-A 2007-217654

[SUMMARY OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0005]

According to the above technology, an acrylic acid-based polymer having small dispersity can be produced, but a small amount of a high-molecular-weight component is included. Therefore, a further improvement has been desired with respect to dispersibility and a reduction in liquid viscosity, for example. An object of the present invention is to provide a method for producing an aqueous solution that is suitable as an inorganic particle dispersant, a water treatment agent, and the like, the aqueous solution including an acrylic acid-based polymer that has small dispersity and has been produced while sufficiently reducing or suppressing the production of a high-molecular-weight polymer as a by-product.

[MEANS FOR SOLVING THE PROBLEMS]

[0006]

The present invention is as follows.

[1] A method for producing an acrylic acid-based polymer aqueous solution continuously using an apparatus that includes a first reactor having a first reaction vessel and a circulation pipe, the first reaction vessel including a raw material feeding means and a stirring means, a monomer including acrylic acid being polymerized in the first reaction vessel in the presence of an initiator and water, and the circulation

pipe being provided outside the first reaction vessel, and connecting an outlet and an inlet that are formed in a wall of the first reaction vessel, the circulation pipe being used to circulate a first reaction liquid that includes a polymer produced in the first reaction vessel, characterized in,

that a cooling means that cools the first reaction liquid is provided to the circulation pipe, and

that the monomer is polymerized, and the first reaction liquid is circulated in a state in which a difference between a temperature of the first reaction liquid at the outlet of the first reaction vessel, and a temperature of the cooled first reaction liquid at the inlet of the first reaction vessel, is 30°C or higher, and a mass ratio of an amount of liquid in an area between the outlet of the first reaction vessel and the cooling means, to an amount of liquid in the first reaction vessel, is 0.050 or less.

[2] The method for producing an acrylic acid-based polymer aqueous solution according to [1] above,

wherein a discharge pipe that discharges the first reaction liquid is connected to the circulation pipe.

[3] The method for producing an acrylic acid-based polymer aqueous solution according to [2] above,

wherein the first reaction liquid discharged through the discharge pipe is neutralized to prepare a second reaction liquid having a pH of 4 to 9.

[4] The method for producing an acrylic acid-based polymer aqueous solution according to [3] above,

wherein the apparatus further includes a second reactor that is connected to the discharge pipe, and

wherein the first reaction liquid is neutralized in the second reactor using an alkaline agent to prepare the second reaction liquid.

[5] The method for producing an acrylic acid-based polymer aqueous solution according to [3] above,

wherein the apparatus further includes a second reactor that is connected to the discharge pipe, and a third reactor that is connected to the second reactor,

wherein polymerization is effected in the second reactor using the first reaction liquid discharged through the discharge pipe, and

wherein a reaction liquid fed from the second reactor is neutralized in the third reactor using an alkaline agent.

In the description, the terms “weight average molecular weight” (hereinafter, referred to as “Mw”) and “number average molecular weight” (hereinafter, referred to as “Mn”) refer to standard sodium polyacrylate-equivalent values determined by gel permeation chromatography (hereinafter, referred to as “GPC”). The term “(meth)acryl” used herein refers to “acryl” and “methacryl”.

[EFFECTS OF THE INVENTION]

[0007]

According to the present invention, it is possible to efficiently produce an aqueous solution including an acrylic acid-based polymer having small dispersity (Mw/Mn) while sufficiently reducing or suppressing the production of a high-molecular-weight polymer as a by-product. Therefore, it is

possible to also efficiently produce an aqueous solution including a homopolymer or a copolymer having a structural unit derived from acrylic acid, as well as an aqueous solution including an acrylic acid-based polymer that is a polymer salt obtained by neutralizing some or all of the carboxy groups derived from acrylic acid using an alkaline agent, and having the above properties with respect to the molecular weight. An acrylic acid-based polymer aqueous solution obtained by the production method of the present invention is suitable as an inorganic particle dispersant, a water treatment agent, and the like.

[BRIEF DESCRIPTION OF THE DRAWING]

[0008]

FIG. 1 is a schematic view illustrating the configuration of the first reactor according to the present invention.

FIG. 2 is a schematic view illustrating the production apparatus used in connection with Examples and Comparative Examples.

[EMBODIMENTS FOR CARRYING OUT THE INVENTION]

[0009]

The present invention provides a method that continuously produces an acrylic acid-based polymer aqueous solution using an apparatus (hereinafter referred to as “production apparatus”) that includes a first reactor 10 (see FIG. 1) having a first reaction vessel 11 and a circulation pipe 20, the first reaction vessel 11 including a raw material feeding means 13 and a stirring means 12, a monomer including acrylic acid being polymerized in the first reaction vessel 11 in the presence of an initiator and water, and the circulation pipe 20 being provided outside the first reaction vessel 11, and connecting an outlet 15 and an inlet 17 that are formed in a wall of the first reaction vessel 11, the circulation pipe 20 being used to circulate a first reaction liquid including a polymer produced in the first reaction vessel 11, wherein a cooling means 25 that cools the first reaction liquid is provided to the circulation pipe 20, and the monomer is polymerized, and the first reaction liquid is circulated in a state in which the difference between the temperature of the first reaction liquid at the outlet 15 of the first reaction vessel 11, and the temperature of the cooled first reaction liquid at the inlet 17 of the first reaction vessel 11, is 30°C or more, and the mass ratio of the amount of liquid in an area between the outlet 15 of the first reaction vessel 11 and the cooling means 25, to the amount of liquid in the first reaction vessel 11, is 0.050 or less, for example. The present invention thus produces an aqueous solution that includes an acrylic acid-based polymer having a dispersity (M_w/M_n) preferably from 1.8 to 2.4 and more preferably from 2.0 to 2.2, and having a solid content preferably from 25% to 55% by mass and more preferably from 35% to 45% by mass.

[0010]

The monomer used in connection with the present invention may include only acrylic acid, or may include acrylic acid and other polymerizable unsaturated compound (hereinafter may be referred to as “other monomer”). Examples of the other polymerizable unsaturated compound include a salt of

acrylic acid; an unsaturated monocarboxylic acid having 4 or more carbon atoms, and a salt thereof; an unsaturated dicarboxylic acid, an anhydride thereof, and a salt thereof; an alkyl (meth)acrylate, a hydroxyalkyl (meth)acrylate, an amide group-containing polymerizable unsaturated compound, a sulfonic acid group-containing polymerizable unsaturated compound, and the like. These compounds may be used singly or in combination of two more types thereof. The salt may be an alkali metal salt such as sodium salt and potassium salt, an alkaline-earth metal salt such as calcium salt and magnesium salt, an ammonium salt, an organic amine salt (e.g., monoethanolamine salt and triethanolamine salt), or the like. When acrylic acid and other monomer are used in combination, acrylic acid is used in an amount of preferably 50% or more by mass and more preferably 80% or more by mass.

Therefore, an acrylic acid-based polymer obtained using the above monomer may be polyacrylic acid or a salt thereof, a copolymer of acrylic acid and other monomer or a salt thereof, or the like. The production method of the present invention produces a first reaction liquid including a polymer having a dispersity (M_w/M_n) within the preferable range by means of the polymerization step that utilizes the first reactor. Even when the polymer included in the first reaction liquid is subjected to a publicly known modification step, the resulting polymer (that falls under the term “acrylic acid-based polymer” used herein) also has a dispersity (M_w/M_n) within the preferable range. For example, when the modification step is a neutralization step, a polymer included in the resulting reaction liquid (second reaction liquid) also has a dispersity (M_w/M_n) within the preferable range.

[0011]

The initiator used in the present invention is not particularly limited, but is preferably a water-soluble compound. Examples of the initiator include an azo compound, a persulfate, hydrogen peroxide, an organic peroxide, and the like. An amount of the initiator to be used is preferably in a range from 0.1 to 3.0 parts by mass, more preferably from 0.3 to 2.0 parts by mass, and further preferably from 0.5 to 1.5 parts by mass based on 100 parts by mass of the monomer.

[0012]

The production method of the present invention utilizes, as mentioned above, the production apparatus that includes the first reactor having a specific configuration.

The first reactor is described below with reference to FIG. 1. The first reactor 10 illustrated in FIG. 1 is not limited to the configuration described herein. The first reactor 10 may appropriately include other element that is not illustrated in FIG. 1.

[0013]

The first reaction vessel 11 is a vessel in which a monomer including acrylic acid is polymerized in the presence of the initiator and water. The first reaction vessel 11 includes the raw material feeding means 13 and the stirring means 12. The raw material feeding means 13 is a means that feeds the monomer, the initiator, a chain transfer agent, water, an organic solvent, and the like to the first reaction vessel 11. Each raw material is normally fed separately when producing an acrylic acid-based polymer

aqueous solution, but specific components may be fed in combination. A feeding method for each raw material is not particularly limited. Each raw material may be fed to the first reaction vessel 11 either continuously or intermittently. The monomer is used so that the concentration of the acrylic acid-based polymer in the desired acrylic acid-based polymer aqueous solution is about 30% to 60% by mass.

The monomer is normally polymerized while maintaining a constant temperature, and the first reaction vessel 11 may include a temperature adjustment means that adjusts the temperature of the raw material or the reaction liquid, a reflux condenser means, and the like. It is preferable that the temperature adjustment means have a structure that covers the side wall and the bottom wall of the first reaction vessel 11.

[0014]

The circulation pipe 20 that is used to circulate the first reaction liquid including the polymer produced in the first reaction vessel 11, is provided outside the first reaction vessel 11. The circulation pipe 20 connects the outlet 15 and the inlet 17 that are formed in the wall of the first reaction vessel 11. The circulation pipe 20 includes a cooling means 25 for decreasing the temperature of the first reaction liquid that has been fed from the first reaction vessel 11, and returns the cooled first reaction liquid to the first reaction vessel 11 through the inlet 17. The first reaction liquid is circulated through the circulation pipe 20 using a pump that is not illustrated in FIG. 1. The position of the pump is not particularly limited. The pump may be provided to a pipe 21 that is situated between the outlet 15 of the first reaction vessel 11 and the cooling means 25, or a pipe 23 that is situated between the cooling means 25 and the inlet 17 of the first reaction vessel 11. The pump is preferably provided to the pipe 21.

As the cooling means 25, a plate heat exchanger, a double-pipe exchanger, a multi-pipe heat exchanger, a spiral heat exchanger, or the like may be used.

A temperature-keeping means for keeping the temperature of the first reaction liquid that flows through the circulation pipe 20 may be provided outside the pipes 21 and 23 included in the circulation pipe 20.

The circulation pipe 20 may include a discharge pipe (not illustrated in FIG. 1) that discharges the first reaction liquid (i.e., an aqueous solution that includes an acrylic acid-based polymer having a dispersity (M_w/M_n) within the preferable range). It is preferable that the discharge pipe be provided to branch from the pipe 21.

[0015]

In the embodiment illustrated in FIG. 1, the outlet 15 that discharges the first reaction liquid is provided to the bottom wall of the first reaction vessel 11, but the position of the outlet 15 is not limited thereto. For example, the outlet 15 may be provided to the side wall of the first reaction vessel 11. In this case, it is preferable that the outlet 15 be provided to the lower part of the first reaction vessel 11. Additionally, the inlet 17 through which the first reaction liquid that has been cooled using the cooling means 25 is returned to the first reaction vessel 11, is provided to the upper side wall of the first reaction

vessel 11, but the position of the inlet 17 is not limited thereto. The inlet 17 may be provided to the top wall of the first reaction vessel 11. In the embodiment illustrated in FIG. 1, the inlet 17 is provided at a position that is higher than the liquid level in the first reaction vessel 11, but the position of the inlet 17 is not limited thereto.

The number of circulation pipes 20 included in the first reactor 10 may be 1, or 2 or more.

[0016]

Next, the production method utilizing the production apparatus that includes the first reactor 10 is described.

A monomer, an initiator, a chain transfer agent, water, an organic solvent, and the like are continuously (or intermittently) fed to the first reaction vessel 11 from the raw material feeding means 13, and the monomer is polymerized while stirring the mixture by operating (driving) the stirring means 12. In the present invention, it is preferable to feed the raw material, polymerize the monomer, and circulate the first reaction liquid while maintaining the amount of the raw material or the reaction liquid in the first reaction vessel 11 to be almost constant.

The polymerization temperature is appropriately set taking account of a type of monomer and a type of initiator, but is preferably in a range from 60°C to 100°C, and more preferably from 70°C to 90°C. In order to continuously produce an aqueous solution that includes an acrylic acid-based polymer having small dispersity while reducing or suppressing the production of a high-molecular-weight polymer as a by-product, a difference between a temperature of the first reaction liquid at the outlet 15 and a temperature of the first reaction liquid (that has been cooled) at the inlet 17 is set to 30°C or more, preferably in a range from 30°C to 60°C, and more preferably from 35°C to 55°C. The temperature of the liquid (raw material or reaction liquid) in the first reaction vessel 11 easily changes along with polymerization of the monomer that is fed continuously. A change in the temperature of the liquid (raw material or reaction liquid) in the first reaction vessel 11 is reduced or suppressed by cooling the first reaction liquid that flows through the circulation pipe 20, and returning the cooled first reaction liquid to the first reaction vessel 11. A known temperature adjustment device such as a jacket and an internal coil may also be used. A flow rate of the first reaction liquid that flows through the circulation pipe 20 is not particularly limited. A feed rate of the first reaction liquid that has been cooled and fed to the first reaction vessel 11 through the inlet 17 is set to preferably in a range from 0.1 to 20 parts per minute, more preferably from 0.2 to 10 parts per minute, and further preferably from 0.5 to 5 parts per minute based on 100 parts of a total amount of the raw material or the reaction liquid in the first reaction vessel 11, from a viewpoint of smooth polymerization.

[0017]

It is possible to produce an aqueous solution that includes an acrylic acid-based polymer having small dispersity while reducing or suppressing the production of a high-molecular-weight polymer as a by-product, by setting the mass ratio of the amount of liquid (i.e., the amount of first reaction liquid) in

the pipe 21 that is situated between the outlet 15 and the cooling means 25, to the amount of liquid (i.e., the amount of raw material or reaction liquid) in the first reaction vessel 11, to 0.050 or less, preferably in a range from 0.001 to 0.040, and more preferably from 0.005 to 0.020. If the mass ratio exceeds 0.050, the dispersity of the acrylic acid-based polymer may be increased, and a high-molecular-weight polymer (by-product) may be produced to a considerable extent, being unfavorable.

[0018]

In the production method of the present invention, a stirring power consumption per cubic meter (m^3) of the reaction liquid that is calculated from the power consumption from which the internal loss of a motor that drives the stirring means 12 is subtracted, and the amount of reaction liquid, is preferably in a range from 0.5 to 3.0 kW/m^3 , and more preferably from 1.0 to 2.0 kW/m^3 . When the stirring power consumption is within the above range, it is possible to produce an aqueous solution that includes an acrylic acid-based polymer having small dispersity while reducing or suppressing the production of a high-molecular-weight polymer as a by-product.

An average residence time of the liquid in the first reaction vessel 11 until completion of polymerization of the monomer fed from the raw material feeding means 13, is appropriately set taking account of a feed rate of the raw material, an internal volume of the first reaction vessel 11, and the like, but is preferably in a range from 0.5 to 4.0 hours, more preferably from 1.0 to 3.0 hours.

[0019]

According to the present invention, an acrylic acid-based polymer aqueous solution in which the content of a high-molecular-weight polymer is reduced can be obtained. A high-molecular-weight polymer having a molecular weight of 70,000 or more is not preferable for an inorganic particle dispersant, and a water treatment agent, for example, from viewpoints of dispersibility and liquid viscosity reduction. The present invention can reduce the content of a high-molecular-weight polymer to preferably 0.2% or less by mass, and more preferably 0.1% or less by mass.

[0020]

After producing an aqueous solution (first reaction liquid) that includes an acrylic acid-based polymer having small dispersity using the first reactor 10, the first reaction liquid (unneutralized aqueous solution) is collected through the discharge pipe provided to the circulation pipe 20, and subjected to a neutralization step to obtain a second reaction liquid that includes an acrylic acid-based polymer in which some or all of the carboxy groups have been converted into $-\text{COOM}^1$ (wherein M^1 is Na, K, NH_4 , or the like). When the first reaction liquid is discharged through the discharge pipe, the first reaction liquid may be fed to a second reactor (not illustrated in FIG. 1), and subjected to the neutralization step, for example.

A method for the neutralization step is not particularly limited. The neutralization step is preferably performed using an alkaline substance such as a hydroxide or a carbonate of an alkali metal (e.g., sodium and potassium); a hydroxide or a carbonate of an alkaline-earth metal (e.g., calcium and

magnesium): ammonia; and an organic amine (e.g., monoethanolamine, diethanolamine, and triethanolamine), or an aqueous solution prepared by dissolving the alkaline substance in water. A pH of the neutralized solution is appropriately set taking account of the intended use of the acrylic acid-based polymer aqueous solution, and the like, but is normally in a range from 4 to 9.

[0021]

Hereinafter, a method for producing an acrylic acid-based polymer aqueous solution that is particularly suitable as an inorganic particle dispersant or a water treatment agent using the production apparatus illustrated in FIG. 2 is described. An acrylic acid-based polymer included in the aqueous solution is a neutralized product of a polymer produced in the presence of an initiator and a chain transfer agent, and is a salt of an acrylic acid-based polymer having an Mw preferably from 3,000 to 10,000, and more preferably from 4,000 to 8,000.

Examples of the chain transfer agent include hypophosphorous acid and a salt thereof, phosphorous acid and a salt thereof, sulfurous acid and a salt thereof, a compound having a thiol group, isopropyl alcohol, and the like. An amount of the chain transfer agent to be used is preferably in a range from 1 to 30 parts by mass, more preferably from 3 to 20 parts by mass, and further preferably from 5 to 10 parts by mass based on 100 parts by mass of the monomer.

[0022]

A production apparatus 1 illustrated in FIG. 2 is one having a structure in which a first reactor 10, a second reactor 30, and a third reactor 50 are connected in this order. For example, polymerization of a monomer is completed in the first reactor 10 and the second reactor 30, and the resulting polymer is neutralized in the third reactor 50 using an alkaline agent.

The first reactor 10 includes, in addition to the elements illustrated in FIG. 1, a discharge pipe 29 branching from the pipe 21 included in the circulation pipe 20. Part of the first reaction liquid produced using the first reaction vessel 11 is fed to the cooling means 25, cooled, and returned to the first reaction vessel 11 through the pipe 23, and the remainder of the first reaction liquid is fed to the second reactor 30 through the discharge pipe 29.

The second reactor 30 includes a second reaction vessel 31 having a stirring means 32. The second reactor 30 may further include a temperature adjustment means for adjusting a temperature of a liquid in the second reaction vessel 31, a reflux condenser means, and the like. An acrylic acid-based polymer aqueous solution (unneutralized aqueous solution) produced using the second reactor 30 is fed to the third reactor 50 through an outlet 35 that is formed in the wall (bottom wall in the example illustrated in FIG. 2) of the second reactor 30, and a discharge pipe 39.

The third reactor 50 includes a third reaction vessel 51 having a stirring means 52 and an alkaline agent feeding means 53. The third reactor 50 may further include a temperature adjustment means for adjusting the temperature of a liquid in the third reaction vessel 51, a reflux condenser means, and the like. An obtained neutralized solution in the third reactor 50 is discharged through an outlet 55

that is formed in the wall (bottom wall in the embodiment illustrated in FIG. 2) of the third reactor 50.
[0023]

It is preferable to provide the first reaction vessel 11 and the second reaction vessel 31 with an acrylic acid-based polymer aqueous solution that has a solid content close to that of the desired acrylic acid-based polymer in order to ensure smooth production.

Subsequently, a monomer containing acrylic acid, an initiator, and a chain transfer agent are fed to the first reaction vessel 11 provided with the acrylic acid-based polymer aqueous solution, and the monomer is polymerized. The monomer can be completely polymerized using the first reactor 10 as described above with reference to FIG. 1, by effecting polymerization under the conditions according to the present invention by utilizing the circulation pipe 20. However, since a small amount of unreacted monomer may be included in the first reaction liquid that is fed to the second reactor 30 through the discharge pipe 29 that branches from the pipe 21 included in the circulation pipe 20 that is included in the first reactor 10, polymerization is effected in the second reactor 30 so that such an unreacted monomer is reliably polymerized. Part of the first reaction liquid produced in the first reaction vessel 11 is cooled with the cooling means 25, returned to the first reaction vessel 11, and used for temperature adjustment or polymerization that is effected using the first reaction vessel 11, as described above. The first reaction liquid discharged through the outlet 15 is not particularly limited but is returned to the first reaction vessel 11 in a range preferably from 30% to 90% by mass, and more preferably from 55% to 85% by weight in order to smoothly produce an acrylic acid-based polymer having small dispersity, and smoothly discharge the acrylic acid-based polymer aqueous solution introduced into the first reaction vessel 11 in advance. It is possible to improve the polymerization conversion rate by circulating the first reaction liquid, and polymerizing the monomer while applying an average residence time within the above range.
[0024]

When polymerization of the monomer starts in the first reaction vessel 11, part of the first reaction liquid is fed to the second reaction vessel 31 included in the second reactor 30 through the discharge pipe 29. Since another acrylic acid-based polymer aqueous solution or the like has been introduced into the second reaction vessel 31 in advance, a mixture with the first reaction liquid fed to the second reaction vessel 31 is obtained in the initial stage of production, and fed to the third reaction vessel 51 included in the third reactor 50 through the outlet 35. Since an acrylic acid-based polymer aqueous solution having the desired solid content is obtained in the first reaction vessel 11 after the average residence time has elapsed, the acrylic acid-based polymer aqueous solution that has been introduced into the second reaction vessel 31 in advance can be discharged smoothly by feeding the aqueous solution to the second reaction vessel 31. The average residence time of a liquid in the second reaction vessel 31 is appropriately set taking account of the volume of the acrylic acid-based polymer aqueous solution introduced in advance, the feed rate of the first reaction liquid that is fed to the second reaction vessel 31, and the like so that unreacted monomer is reliably polymerized. The M_w of the acrylic acid-based

polymer produced in the second reactor 30 is preferably in a range from 3,000 to 10,000, and more preferably from 4,000 to 8,000. The dispersity (M_w/M_n) is preferably in a range from 1.8 to 2.4, and more preferably from 2.0 to 2.2.

[0025]

After that, the aqueous solution of the acrylic acid-based polymer having preferable properties is fed to the third reaction vessel 51 included in the third reactor 50 through the discharge pipe 39. In the third reaction vessel 51, an alkaline agent is fed from the alkaline agent feeding means 53, and a neutralization reaction is effected while stirring to obtain an aqueous solution having the desired pH.

[0026]

The above production is an embodiment in which the neutralization step is performed using the third reactor 50. The neutralization step may be performed using the second reactor 30 in which unreacted monomer is continuously polymerized, or may be performed using both the second reactor 30 and the third reactor 50. When the neutralization step can be completed using the second reactor 30, the third reactor 50 need not necessarily be used.

[0027]

An acrylic acid-based polymer aqueous solution produced by the present invention is suitable as an inorganic particle dispersant, a water treatment agent (i.e., an agent that reduces or suppresses the formation, precipitation, or deposition of scale), and the like.

When the acrylic acid-based polymer aqueous solution is used as an inorganic particle dispersant, the acrylic acid-based polymer aqueous solution is used directly as the inorganic particle dispersant. The acrylic acid-based polymer aqueous solution may optionally be used in combination with other component such as defoamer and preservative. Examples of the inorganic particle include particles formed of calcium carbonate, kaolin, talc, clay, silica, aluminum hydroxide, zeolite, titanium dioxide, and the like.

When the acrylic acid-based polymer aqueous solution is used as a water treatment agent, the aqueous solution may be used directly as the water treatment agent, or may optionally be used in combination with other component such as a scale inhibitor (e.g., polymaleic acid or a salt thereof, a (meth)acrylic acid-based copolymer, and a styrene-maleic acid-based copolymer), a disinfectant, an anti-corrosion agent, a slime inhibitor, and a defoamer. It is possible to reduce or suppress a decrease in heat exchange efficiency, pipe clogging, and the like that may occur in a cooling water system, a boiler water system, a seawater desalination plant, and the like, by utilizing such a water treatment agent.

[EXAMPLES]

[0028]

Hereinafter, the present invention is specifically described using Examples. The present invention is not limited to the Examples. In the following description, “%” is based on mass unless otherwise indicated.

[0029]

1. Production apparatus for acrylic acid-based polymer aqueous solution

In the following Experimental Examples, an acrylic acid-based polymer aqueous solution having a pH of 7 was produced using the apparatus 1 illustrated in FIG. 2 having a structure in which the first reactor 10, the second reactor 30, and the third reactor 50 are connected in this order.

The first reactor 10 includes a bottomed cylindrical container (first reaction vessel) 11 in which polymerization is effected, a stirrer 12, a raw material feed pipe 13 that feeds a monomer, an initiator, a chain transfer agent, and the like, and a condenser (not illustrated in FIG. 2), and further includes a jacket (i.e., temperature adjustment means) (not illustrated in FIG. 2) that is provided to cover the outer periphery of the cylindrical container 11, and adjusts the temperature of a liquid in the cylindrical container 11 using a cooling water, and a circulation pipe 20 through which a reaction liquid including an acrylic acid-based polymer circulates, and which is provided outside the cylindrical container 11 so as to connect an outlet 15 that is formed in the bottom wall of the cylindrical container 11, and an inlet 17 that is formed in the side wall of the cylindrical container 11 at a position that is higher than the liquid level. The circulation pipe 20 sequentially includes a pump 27, a T-shaped pipe that is provided with a discharge pipe 29 having a valve that feeds a liquid to the second reaction vessel 31 included in the second reactor 30, and a heat exchanger 25 that cools the reaction liquid that circulates through the circulation pipe 20 using a cooling water, the pump 27, the T-shaped pipe, and the heat exchanger 25 being provided between the outlet 15 and the inlet 17. Thermometers (not illustrated in FIG. 2) for measuring temperatures of the reaction liquid are provided to the outlet 15 and the inlet 17 of the cylindrical container 11 to which the circulation pipe 20 is provided.

The second reactor 30 includes a bottomed cylindrical container (second reaction vessel) 31, a stirrer 32, a condenser (not illustrated in FIG. 2), and a jacket (not illustrated in FIG. 2), and further includes an outlet 35 that is formed in the bottom wall of the cylindrical container 31, and feeds a reaction liquid containing an acrylic acid-based polymer to the third reactor 50, and a pump 37 that is provided between the outlet 35 and a discharge pipe 39 that is connected to the third reaction vessel 51 included in the third reactor 50.

The third reactor 50 includes a bottomed cylindrical container (third reaction vessel) 51, a stirrer 52, a pH-adjusting agent feed pipe 53 that feeds a pH-adjusting agent (alkaline agent) into the container 51, a condenser (not illustrated in FIG. 2), and a jacket (not illustrated in FIG. 2), and further includes an outlet 55 that is formed in the bottom wall of the cylindrical container 51, and used to discharge and collect an acrylic acid-based polymer aqueous solution.

[0030]

2. Production of acrylic acid-based polymer aqueous solution (1)

Example 1

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,200 kg of

an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 80°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 80°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (80°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 43°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 20 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,200 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 92 minutes. A stirring power consumption that was calculated from the power consumption from which the internal loss of the motor of the stirrer 12 was subtracted, and the amount of reaction liquid, was 1.1 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 80°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 2,200 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,200 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 92 minutes.

After that, water and a 48% sodium hydroxide aqueous solution (hereinafter may be referred to as “48%NaOH”) were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 80°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,200 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55

when the amount of liquid in the third reaction vessel 51 had exceeded 2,200 kg.

After performing the above operation for 20 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E1) (solid content: 40%) including an acrylic acid-based polymer (see Table 1).

[0031]

The acrylic acid-based polymer was subjected to gel permeation chromatography (GPC) under the following conditions. The acrylic acid-based polymer had an Mw of 6,000 and a dispersity (Mw/Mn) of 2.2. A content of a polymer having a molecular weight of 70,000 or more determined by molecular weight fraction calculations was 0.01% based on the total amount of the acrylic acid-based polymer.

(GPC measurement conditions)

Device: HLC-8020 system manufactured by Tosoh Corporation

Detection: RI

Column: G4000PW×l, G3000PW×l, and G2500PW×l (manufactured by Tosoh Corporation) (these columns were connected)

Eluent: 0.1 M-NaCl+phosphate buffer (pH: 7)

Standard: sodium polyacrylate manufactured by Sowa Scientific Corporation

[0032]

Example 2

An aqueous solution (E2) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 1, except that the stirring power consumption was changed to 0.7 kW/m³, and then the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0033]

Example 3

An aqueous solution (E3) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 1, except that a reaction liquid that had been cooled to 49°C using the heat exchanger 25 was fed to the first reaction vessel 11, and then the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0034]

Example 4

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 1,800 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 80°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected

while maintaining the temperature of the mixture at 80°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (80°C) was extracted at a flow rate of 124 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (99 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 44°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 20 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 1,800 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 76 minutes. A stirring power consumption that was calculated from the power consumption from which the internal loss of the motor of the stirrer 12 was subtracted, and the amount of reaction liquid, was 1.0 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 80°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 1,800 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 1,800 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 76 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 80°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 1,800 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 1,800 kg.

After performing the above operation for 20 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E4) (solid content: 40%) including an acrylic acid-based polymer, and the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0035]

Example 5

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,200 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 80°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 80°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (80°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 42°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 80 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,200 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 95 minutes. A stirring power consumption that was calculated from the power consumption from which the internal loss of the motor of the stirrer 12 was subtracted, and the amount of reaction liquid, was 1.1 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 80°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 2,200 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,200 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 92 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 80°C.

The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,200 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,200 kg.

After performing the above operation for 20 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E5) (solid content: 40%) including an acrylic acid-based polymer, and the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0036]

Example 6

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,200 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 80°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 80°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (80°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 43°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 20 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 180 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,200 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 97 minutes. A stirring power consumption that was calculated from the power consumption from which the internal loss of the motor of the stirrer 12 was subtracted, and the amount of reaction liquid, was 1.1 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 80°C, and maintaining the amount of liquid in the second

reaction vessel 31 to be 2,200 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,200 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 92 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 80°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,200 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,200 kg.

After performing the above operation for 20 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E6) (solid content: 40%) including an acrylic acid-based polymer, and the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0037]

Comparative Example 1

An aqueous solution (C1) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 1, except that a reaction liquid that had been cooled to 58°C using the heat exchanger 25 was fed to the first reaction vessel 11, and then the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0038]

Comparative Example 2

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,200 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 80°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 80°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (80°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 42°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25

kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 160 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,200 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 98 minutes. A stirring power consumption that was calculated from the power consumption from which the internal loss of the motor of the stirrer 12 was subtracted, and the amount of reaction liquid, was 1.1 kW/m^3 .

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 80°C , and maintaining the amount of liquid in the second reaction vessel 31 to be 2,200 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,200 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 92 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 80°C . The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,200 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,200 kg.

After performing the above operation for 20 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (C2) (solid content: 40%) including an acrylic acid-based polymer, and the acrylic acid-based polymer was subjected to GPC (see Table 1).

[0039]

TABLE 1

		Example						Comparative Example	
		1	2	3	4	5	6	1	2
First reactor	60% acrylic acid aqueous solution	(kg/min)	20	20	20	20	20	20	20
	15% sodium persulfate aqueous solution	(kg/min)	1.2	1.2	1.2	1.2	1.2	1.2	1.2
	30% sodium hydrogen sulfite aqueous solution	(kg/min)	3.5	3.5	3.5	3.5	3.5	3.5	3.5
	Amount (a) of liquid discharged to circulation pipe	(kg/min)	62	62	62	124	62	62	62
	Amount (b) of liquid fed to second reactor	(kg/min)	25	25	25	25	25	25	25
	(a)÷(b)		2.5	2.5	2.5	5.0	2.5	2.5	2.5
	Amount (c) of liquid in first reaction vessel	(kg)	2,200	2,200	2,200	1,800	2,200	2,200	2,200
	Amount (d) of liquid in area between outlet and heat exchanger	(kg)	20	20	20	20	80	20	160
	Amount (e) of liquid in area between heat exchanger and inlet	(kg)	60	60	60	60	60	60	60
	(d)÷(e)		0.009	0.009	0.009	0.011	0.036	0.009	0.073
Second reactor	(e)÷(c)		0.027	0.027	0.027	0.033	0.027	0.082	0.027
	Average residence time	(min)	92	92	92	76	95	97	92
	Temperature of liquid in first reaction vessel	(°C)	80	80	80	80	80	80	80
	Temperature (T1) of liquid at outlet	(°C)	80	80	80	80	80	80	80
	Temperature (T2) of liquid at inlet	(°C)	43	43	49	44	42	43	58
	(T1)-(T2)	(°C)	37	37	31	36	38	37	22
	Liquid temperature	(°C)	80	80	80	80	80	80	80
	Average residence time	(min)	92	92	92	76	92	92	92
	Acrylic acid-based polymer aqueous solution		E1	E2	E3	E4	E5	E6	C1
	Solid content	(%)	40	40	40	40	40	40	40
Acrylic acid-based polymer aqueous solution	pH		7	7	7	7	7	7	7
	Mw		6,000	6,300	6,200	6,300	6,200	6,100	6,500
	Mw/Mn		2.2	2.4	2.4	2.2	2.4	2.3	2.6
	Content of polymer having molecular weight of 70,000 or more	(%)	0.01	0.07	0.07	0.02	0.06	0.04	0.30

[0040]

3. Production of acrylic acid-based polymer aqueous solution (2)

Example 7

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,900 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 85°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 85°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (85°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 46°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 20 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,900 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 121 minutes. A stirring power consumption was 1.0 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 85°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 2,900 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,900 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 121 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 85°C.

The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,900 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,900 kg.

After performing the above operation for 24 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E7) (solid content: 40%) including an acrylic acid-based polymer (see Table 2).

The acrylic acid-based polymer included in the acrylic acid-based polymer aqueous solution (E7) was subjected to GPC in the same manner as those in Example 1. The results (M_w and the like) are listed in Table 2.

[0041]

Example 8

An aqueous solution (E8) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 7, except that the stirring power consumption was changed to 0.7 kW/m^3 , and then the acrylic acid-based polymer was subjected to GPC (see Table 2).

[0042]

Example 9

An aqueous solution (E9) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 7, except that a reaction liquid that had been cooled to 54°C using the heat exchanger 25 was fed to the first reaction vessel 11, and then the acrylic acid-based polymer was subjected to GPC (see Table 2).

[0043]

Example 10

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,900 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an M_w of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 85°C .

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 85°C , and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (85°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 46°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided

to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 80 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,900 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 123 minutes. A stirring power consumption was 1.0 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 85°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 2,900 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,900 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 121 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 85°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,900 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,900 kg.

After performing the above operation for 24 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E10) (solid content: 40%) including an acrylic acid-based polymer (see Table 2).

The acrylic acid-based polymer included in the acrylic acid-based polymer aqueous solution (E10) was subjected to GPC in the same manner as those in Example 1. The results (Mw and the like) are listed in Table 2.

[0044]

Example 11

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,900 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an Mw of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 85°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2

kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 85°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (85°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 46°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 20 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 180 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,900 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 126 minutes. A stirring power consumption was 1.0 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 85°C, and maintaining the amount of liquid in the second reaction vessel 31 to be 2,900 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,900 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 121 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 85°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,900 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,900 kg.

After performing the above operation for 24 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (E11) (solid content: 40%) including an acrylic acid-based polymer (see Table 2).

The acrylic acid-based polymer included in the acrylic acid-based polymer aqueous solution (E11) was subjected to GPC in the same manner as those in Example 1. The results (M_w and the like) are listed in Table 2.

[0045]

Comparative Example 3

An aqueous solution (C3) (solid content: 40%) including an acrylic acid-based polymer was produced in the same manner as those in Example 7, except that a reaction liquid that had been cooled to 63°C using the heat exchanger 25 was fed to the first reaction vessel 11, and then the acrylic acid-based polymer was subjected to GPC (see Table 2).

[0046]

Comparative Example 4

The first reaction vessel 11 and the second reaction vessel 31 were both charged with 2,900 kg of an aqueous solution (solid content: 40%) including polyacrylic acid having an M_w of 6,000, and the temperature of the aqueous solution was maintained at a temperature of 85°C.

A 60% acrylic acid aqueous solution (20 kg/min), a 15% sodium persulfate aqueous solution (1.2 kg/min), and a 30% sodium hydrogen sulfite aqueous solution (3.5 kg/min) were respectively fed to the first reaction vessel 11 using the raw material feed pipe 13, and a polymerization reaction was effected while maintaining the temperature of the mixture at 85°C, and operating the stirrer 12 at a rotational speed of 80 rpm. Simultaneously, a reaction liquid (85°C) was extracted at a flow rate of 62 kg/min through the outlet 15 of the first reaction vessel 11 by adjusting the output of the pump 27 provided to the circulation pipe 20, and passed through the circulation pipe 20. Part of the reaction liquid (37 kg/min) was cooled using the heat exchanger 25, and the reaction liquid of 46°C was fed to the first reaction vessel 11 through the inlet 17 of the first reaction vessel 11. The remainder of the reaction liquid (25 kg/min) extracted through the outlet 15 was fed to the second reactor 30 by adjusting the valve provided to the discharge pipe 29.

A capacity of the circulation pipe 20 (connecting the outlet 15 and the inlet 17 of the first reaction vessel 11) in an area between the outlet 15 of the first reaction vessel 11 and the heat exchanger 25 was 160 kg. A capacity of the circulation pipe 20 in an area between the heat exchanger 25 and the inlet 17 was 60 kg. A polymerization reaction was effected under the above conditions while maintaining the amount of liquid in the first reaction vessel 11 to be 2,900 kg. An average residence time of the reaction liquid in the first reaction vessel 11 and the circulation pipe 20 was 126 minutes. A stirring power consumption was 1.0 kW/m³.

The reaction liquid that was fed to the second reactor 30 through the discharge pipe 29 at a flow rate of 25 kg/min, and an aqueous solution containing polyacrylic acid that was introduced into the second reactor 30 in advance, were mixed by operating the stirrer 32 at a rotational speed of 80 rpm while maintaining the temperature of the mixture at 85°C, and maintaining the amount of liquid in the second

reaction vessel 31 to be 2,900 kg, to polymerize the remaining acrylic acid. The amount of liquid in the second reaction vessel 31 was maintained to be 2,900 kg by feeding the reaction liquid to the third reactor 50 through the outlet 35 of the second reaction vessel 31 in the same amount as that (25 kg/min) of the reaction liquid fed from the first reaction vessel 11. An average residence time of the reaction liquid was 121 minutes.

After that, water and a 48%NaOH were respectively fed to the third reactor 50 through the pH-adjusting agent feed pipe 53. A reaction liquid fed from the second reactor 30 was neutralized to have a pH of 7.0 while stirring the mixture, and maintaining the temperature of the mixture at 85°C. The neutralization reaction was effected while maintaining the amount of liquid in the third reaction vessel 51 to be 2,900 kg, and discharging the neutralized solution (acrylic acid-based polymer aqueous solution) through the outlet 55 when the amount of liquid in the third reaction vessel 51 had exceeded 2,900 kg.

After performing the above operation for 24 hours, the neutralized solution was collected through the outlet 55 of the third reaction vessel 51 to obtain an aqueous solution (C4) (solid content: 40%) including an acrylic acid-based polymer (see Table 2).

The acrylic acid-based polymer included in the acrylic acid-based polymer aqueous solution (C4) was subjected to GPC in the same manner as those in Example 1. The results (Mw and the like) are listed in Table 2.

[0047]

TABLE 2

		Example							Comparative Example		
		7	8	9	10	11	3	4			
First reactor	60% acrylic acid aqueous solution	(kg/min)	20	20	20	20	20	20	20	20	20
	15% sodium persulfate aqueous solution	(kg/min)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
	30% sodium hypophosphite aqueous solution	(kg/min)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
	Amount (a) of liquid discharged to circulation pipe	(kg/min)	62	62	62	62	62	62	62	62	62
	Amount (b) of liquid fed to second reactor	(kg/min)	25	25	25	25	25	25	25	25	25
	(a)÷(b)		2.5	2.5	2.5	5.0	2.5	2.5	2.5	2.5	2.5
	Amount (c) of liquid in first reaction vessel	(kg)	2,900	2,900	2,900	2,900	2,900	2,900	2,900	2,900	2,900
	Amount (d) of liquid in area between outlet and heat exchanger	(kg)	20	20	20	80	20	20	20	20	160
	Amount (e) of liquid in area between heat exchanger and inlet	(kg)	60	60	60	60	180	60	60	60	60
	(d)÷(c)		0.007	0.007	0.007	0.028	0.007	0.007	0.007	0.007	0.055
Second reactor	(e)÷(c)		0.021	0.021	0.021	0.021	0.062	0.021	0.021	0.021	0.021
	Average residence time	(min)	121	121	121	123	126	121	121	126	126
	Temperature of liquid in first reaction vessel	(°C)	85	85	85	85	85	85	85	85	85
	Temperature (T1) of liquid at outlet	(°C)	85	85	85	85	85	85	85	85	85
	Temperature (T2) of liquid at inlet	(°C)	46	46	54	46	46	46	63	46	46
	(T1)-(T2)	(°C)	39	39	31	39	39	22	39	39	39
	Liquid temperature	(°C)	85	85	85	85	85	85	85	85	85
	Average residence time	(min)	121	121	121	121	121	121	121	121	121
	polymer aqueous solution		E7	E8	E9	E10	E11	C3	C4	C4	C4
	Solid content	(%)	40	40	40	40	40	40	40	40	40
Acrylic acid-based	pH		7	7	7	7	7	7	7	7	
	Mw		5,000	5,300	5,200	5,200	5,100	5,500	5,500	5,500	
	Mw/Mn		2.1	2.3	2.3	2.3	2.2	2.5	2.5	2.5	
	Content of polymer having molecular weight of 70,000 or more	(%)	0.01	0.06	0.06	0.05	0.04	0.26	0.26	0.26	0.28

[0048]

4. Evaluation of acrylic acid-based polymer aqueous solution

The acrylic acid-based polymer aqueous solutions obtained in Examples 1 to 11 and Comparative Examples 1 to 4 were subjected to the following tests. The results are listed in Table 3.

[0049]

(1) Wet grinding test with ground calcium carbonate

A cylindrical vessel equipped with a stirrer was charged with 7.5 g of the acrylic acid-based polymer aqueous solution, 340 g of ion-exchanged water, and 1,000 g of ground calcium carbonate “No. A Heavy Carbonate” (trade name) manufactured by Maruo Calcium Co., Ltd., and the mixture was lightly and homogeneously stirred. 2,800 g of media (ceramic bead having a diameter of 1 mm) was then added to the cylindrical vessel, and the mixture was stirred at 1,000 rpm for 50 minutes to wet-grind the calcium carbonate. The resulting liquid was passed through a 150-mesh filter cloth, and ion-exchanged water was added to obtain a slurry having a solid content of 75%.

An integrated value under 2.0 μm of the slurry was measured using a particle size distribution analyzer “SediGraph 5120” (trade name) manufactured by Micromeritics.

A viscosity of the slurry immediately after preparation, and a viscosity of the slurry after being allowed to stand at 25°C for 7 days were measured at 25°C and 60 rpm using a Brookfield viscometer.

[0050]

(2) Mixing dispersion test with ground calcium carbonate

A cylindrical vessel equipped with a stirrer was charged with 6.0 g of the acrylic acid-based polymer aqueous solution, 330 g of ion-exchanged water, and 1,000 g of heavy calcium carbonate “Super #2000” (trade name) manufactured by Maruo Calcium Co., Ltd., and the mixture was stirred at 4,000 rpm for 10 minutes to obtain a slurry. A viscosity of the slurry immediately after preparation, and a viscosity of the slurry after being allowed to stand at 25°C for 7 days were measured at 25°C and 60 rpm using a Brookfield viscometer.

[0051]

(3) Mud dispersion test

A 100 mL graduated cylinder was charged with 13 mg of the acrylic acid-based polymer aqueous solution, 1 g of clay “Amazon 88 Non-Predisperse” (trade name) manufactured by Mitsubishi Corporation, and 100 g of ion-exchanged water, and the mixture was stirred for 10 minutes using a magnetic stirrer. After allowing the mixture to stand at 25°C for 18 hours, the supernatant liquid was sampled, and the absorbance at a wavelength of 380 nm was measured. A higher absorbance indicates better clay dispersibility.

[0052]

(4) Calcium carbonate scale reduction/suppression test

The acrylic acid-based polymer aqueous solution was added to 100 mL of a calcium chloride

aqueous solution (200 mg CaCO_3/L) so that the content of the acrylic acid-based polymer was 10 mg. After the addition of 10 g of a 0.2% sodium hydrogen carbonate aqueous solution, the pH of the aqueous solution was adjusted to 8.5 using sodium hydroxide. After allowing the mixture to stand at 60°C for 24 hours, a precipitate was filtered off, and the calcium concentration in the filtrate was determined by EDTA titration to calculate the scale reduction/suppression rate.

[0053]

TABLE 3

		Example										
		1	2	3	4	5	6	7	8	9	10	11
Wet grinding test	Acrylic acid-based polymer aqueous solution	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
	<2.0-μm integrated value (%)	90	90	90	90	90	90	90	90	90	90	90
	Viscosity of slurry immediately after preparation (mPa·s)	210	260	250	220	250	230	190	220	220	220	200
Mixing dispersion test	Viscosity of slurry after 7 days (mPa·s)	1,400	1,800	1,800	1,500	1,700	1,600	1,200	1,800	1,700	1,700	1,400
	Viscosity of slurry immediately after dispersion (mPa·s)	110	120	120	110	110	110	100	160	150	160	150
	Viscosity of slurry after 7 days (mPa·s)	520	640	610	530	620	570	500	690	640	660	600
Mud dispersion test	Absorbance of supernatant liquid	1.3	1.0	1.1	1.3	1.2	1.3	1.3	1.1	1.1	1.2	1.3
Scale reduction/ suppression test	Scale reduction/suppression rate (%)	96	92	94	95	93	95	97	93	93	94	95

TABLE 3 (continued)

	Comparative Example			
	1	2	3	4
Wet grinding test	Acrylic acid-based polymer aqueous solution			
	<2.0-μm integrated value (%)			
	C1	C2	C3	C4
	90	90	90	90
Mixing dispersion test	300	300	260	260
	Viscosity of slurry immediately after preparation (mPa·s)			
	4,100	4,000	3,500	3,700
	Viscosity of slurry after 7 days (mPa·s)			
Mud dispersion test	140	130	170	170
	Viscosity of slurry immediately after dispersion (mPa·s)			
	850	880	960	940
	Viscosity of slurry after 7 days (mPa·s)			
Scale reduction/suppression test	0.8	0.8	0.8	0.8
	Absorbance of supernatant liquid			
	84	84	84	86
	Scale reduction/suppression rate (%)			

[0054]

The following is clear from results in Table 3. Since Comparative Examples 1 and 3 were examples in which a difference between the temperature of the reaction liquid at the outlet of the first reaction vessel, and the temperature of the reaction liquid cooled using the heat exchanger at (immediately in front of) the inlet of the first reaction vessel, was 22°C, the resultant acrylic acid-based polymers had large dispersity (Mw/Mn), and the content of a high-molecular-weight polymer was high. Moreover, satisfactory performance was not obtained in the wet grinding test, mixing dispersion test, mud dispersion test, and scale reduction/suppression test. Since Comparative Examples 2 and 4 were examples in which the mass ratio of the amount of liquid in the circulation pipe in an area between the outlet of the first reaction vessel and the heat exchanger to the amount of liquid in the first reaction vessel was more than 0.050, the resultant acrylic acid-based polymers had large dispersity (Mw/Mn), and the content of a high-molecular-weight polymer was high. Moreover, satisfactory performance was not obtained in the wet grinding test, mixing dispersion test, mud dispersion test, and scale reduction/suppression test.

On the other hand, Examples 1 to 11 were examples leading to the acrylic acid-based polymer aqueous solutions. Since the acrylic acid-based polymers had small dispersity (Mw/Mn), and the content of a high-molecular-weight polymer was low, excellent results were obtained in the wet grinding test, mixing dispersion test, mud dispersion test, and scale reduction/suppression test.

[INDUSTRIAL APPLICABILITY]

[0055]

An acrylic acid-based polymer aqueous solution obtained by the present invention is suitable as an inorganic particle dispersant, a water treatment agent, and the like.

[REFERENCE SIGNS LIST]

[0056]

1: production apparatus, 10: first reactor, 11: first reaction vessel, 12: stirrer (stirring means), 13: raw material feed pipe (raw material feeding means), 15: outlet, 17: inlet, 20: circulation pipe, 21: pipe situated between outlet and heat exchanger (cooling means), 23: pipe situated between heat exchanger (cooling means) and inlet, 25: heat exchanger (cooling means), 27: pump, 29: discharge pipe, 30: second reactor, 31: second reaction vessel, 32: stirrer, 35: outlet, 37: pump, 39: discharge pipe, 50: third reactor, 51: third reaction vessel, 52: stirrer, 53: pH-adjusting agent feed pipe (alkaline agent feeding means), 55: outlet

CLAIMS

1. A method for producing an acrylic acid-based polymer aqueous solution continuously using an apparatus that comprises a first reactor comprising a first reaction vessel and a circulation pipe, the first reaction vessel comprising a raw material feeding means and a stirring means, a monomer comprising acrylic acid being polymerized in the first reaction vessel in the presence of an initiator and water, and the circulation pipe being provided outside the first reaction vessel, and connecting an outlet and an inlet that are formed in a wall of the first reaction vessel, the circulation pipe being used to circulate a first reaction liquid that comprises a polymer produced in the first reaction vessel, characterized in,
 - that a cooling means that cools the first reaction liquid is provided to the circulation pipe, and
 - that the monomer is polymerized, and the first reaction liquid is circulated in a state in which a difference between a temperature of the first reaction liquid at the outlet of the first reaction vessel, and a temperature of the cooled first reaction liquid at the inlet of the first reaction vessel, is 30°C or higher, and a mass ratio of an amount of liquid in an area between the outlet of the first reaction vessel and the cooling means, to an amount of liquid in the first reaction vessel, is 0.050 or less.
2. The method for producing an acrylic acid-based polymer aqueous solution according to claim 1, wherein a discharge pipe that discharges the first reaction liquid is connected to the circulation pipe.
3. The method for producing an acrylic acid-based polymer aqueous solution according to claim 2, wherein the first reaction liquid discharged through the discharge pipe is neutralized to prepare a second reaction liquid having a pH of 4 to 9.
4. The method for producing an acrylic acid-based polymer aqueous solution according to claim 3, wherein the apparatus further comprises a second reactor that is connected to the discharge pipe, and
 - wherein the first reaction liquid is neutralized in the second reactor using an alkaline agent to prepare the second reaction liquid.
5. The method for producing an acrylic acid-based polymer aqueous solution according to claim 3, wherein the apparatus further comprises a second reactor that is connected to the discharge pipe, and a third reactor that is connected to the second reactor,
 - wherein polymerization is effected in the second reactor using the first reaction liquid discharged through the discharge pipe, and
 - wherein a reaction liquid fed from the second reactor is neutralized in the third reactor using an alkaline agent.