

ACRYLIC ACID-BASED COPOLYMER, METHOD FOR PRODUCING SAME AND WATER TREATMENT AGENT

[TECHNICAL FIELD]

[0001]

The present invention relates to an acrylic acid-based copolymer (hereinafter, referred to as “AA/ATBS-based polymer”) that is suitable as a major component of a water treatment agent which exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate, and to a method for producing the same.

[BACKGROUND ART]

[0002]

A copolymer (AA/ATBS-based polymer) including a structural unit derived from acrylic acid or a salt thereof, and a structural unit derived from 2-acrylamido-2-methylpropanesulfonic acid (also referred to as “acrylamido-tert-butylsulfonic acid”) or a salt thereof, is known as a major component of a dispersant for inorganic particles, an agent for reducing or suppressing the formation, precipitation or deposition of a scale, and the like.

For example, Patent Document 1 discloses an AA/ATBS-based polymer that is neutralized (pH: 3.5 to 6.0) using sodium hydroxide. Patent Document 2 discloses an AA/ATBS-based polymer that is neutralized using sodium hydroxide and calcium hydroxide. Patent Document 3 discloses an AA/ATBS-based polymer that further includes a structural unit derived from a monomer that is poorly soluble in water (e.g., phenoxyethyl acrylate). Additionally, Patent Document 4 discloses an AA/ATBS-based polymer that further includes a structural unit derived from ethoxylated tristyrylphenol methacrylate.

[PRIOR TECHNICAL DOCUMENT]

[PATENT DOCUMENT]

[0003]

[Patent Document 1] JP-T 2000-502394

[Patent Document 2] JP-T H6-504939

[Patent Document 3] JP-A 2000-169508

[Patent Document 4] JP-A H11-104479

[SUMMARY OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0004]

However, the AA/ATBS-based polymers disclosed in the above Patent Documents 1 to 4 may not exhibit satisfactory performance when used for a water treatment agent. In particular, the AA/ATBS-based polymers disclosed in the above documents do not exhibit a sufficient effect of reducing or suppressing the formation of a scale due to calcium phosphate. Therefore, an acrylic acid-based copolymer (AA/ATBS-based polymer) that is suitable as a major component of a water treatment agent that exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate, a method for producing the same, and a water treatment agent have been desired.

[MEANS FOR SOLVING THE PROBLEMS]

[0005]

The inventor conducted extensive studies in order to solve the above problem. As a result, the inventor found that a small amount of high-molecular-weight polymer is produced as a by-product when acrylic acid and sodium 2-acrylamido-2-methylpropanesulfonate are polymerized by a known method, and deterioration in capability to reduce or suppress the formation of a scale occurs due to the high-molecular-weight polymer. The inventor found based on this finding that an AA/ATBS-based polymer in which a content of a high-molecular-weight polymer is reduced to be equal to or less than a specific amount exhibits an excellent capability to reduce or suppress the formation of a scale due to calcium phosphate. These findings have led to the completion of the invention.

Further, the inventor also found that a known production method has a problem in that the sodium concentration in the reaction mixture changes during the reaction, and it is impossible to continuously effect polymerization under constant conditions, whereby a high-molecular-weight polymer is produced as a by-product. The inventor found based on this finding that it is possible to efficiently produce an AA/ATBS-based polymer that includes a high-molecular-weight polymer in a very small amount by effecting polymerization while maintaining the sodium concentration in the reaction mixture at a constant level.

[0006]

The present invention is as follows.

[1] An acrylic acid-based copolymer comprising a structural unit (x) derived from acrylic acid or a sodium salt thereof, and a structural unit (y) derived from 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof, the acrylic acid-based copolymer comprising the structural unit (x) and the structural unit (y) in a ratio of 35% to 90% by mass and 10% to 65% by mass, respectively, based on 100% by mass of a total content of the structural unit (x) and the structural unit (y) in the acrylic acid-based copolymer,

wherein the acrylic acid-based copolymer has a weight average molecular weight (Mw) of 2,000

to 30,000, and includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more in an amount of 0.30% or less by mass based on a total amount of polymers.

[2] The acrylic acid-based copolymer according to the above [1], having a polydispersity (M_w/M_n) of 3.5 or less, the polydispersity being a ratio of a weight average molecular weight (M_w) to a number average molecular weight (M_n) of the acrylic acid-based copolymer.

[3] The acrylic acid-based copolymer according to the above [1] or [2], wherein the structural unit (x) is a structural unit derived from a sodium salt of acrylic acid, and the structural unit (y) is a structural unit derived from a sodium salt of 2-acrylamido-2-methylpropanesulfonic acid.

[4] A method for producing the acrylic acid-based copolymer according to any one of the above [1] to [3], comprising polymerizing monomers while continuously supplying the monomers to a reactor, the monomers comprising acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof.

[5] A method for producing the acrylic acid-based copolymer according to any one of the above [1] to [3], the method being implemented using a production apparatus in which three reactors are connected, and comprising polymerizing monomers in a first reactor in the presence of a polymerization initiator while continuously supplying the monomers to the first reactor, the monomers comprising acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof, transferring a reaction mixture from the first reactor to a second reactor that is connected to the first reactor, polymerizing the monomers included in the reaction mixture in the second reactor, transferring a reaction mixture from the second reactor to a third reactor that is connected to the second reactor, and adjusting a pH of a polymer containing liquid to 9 or less in the third reactor.

[6] The method for producing an acrylic acid-based copolymer according to the above [5], wherein the polymerization initiator comprises a persulfate.

[7] The method for producing an acrylic acid-based copolymer according to the above [5] or [6], wherein the pH of the polymer containing liquid is adjusted to a range from 3.0 to 8.0 in the third reactor.

[8] A water treatment agent comprising the acrylic acid-based copolymer according to any one of the above [1] to [3].

[9] The water treatment agent according to the above [8], wherein the acrylic acid-based copolymer has a weight average molecular weight (M_w) of 4,000 to 20,000, includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more in a ratio of 0.05% or less by mass based on a total amount of polymers, and has a polydispersity (M_w/M_n) of 3.5 or less, the polydispersity being the ratio of a weight average molecular weight (M_w) to a number average molecular weight (M_n) of the acrylic acid-based copolymer.

In the description, the terms “weight average molecular weight (hereinafter, referred to as “ M_w ”) and “number average molecular weight” (hereinafter, referred to as “ M_n ”) 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]

The acrylic acid-based copolymer (AA/ATBS-based polymer) of the present invention has a more uniform composition, and is therefore suitable as a major component of an agent that reduces or suppresses the formation, precipitation or deposition of a scale, a dispersant for inorganic particles, and the like. In particular, since the acrylic acid-based copolymer is characterized in that the contents of the structural unit (x) and the structural unit (y) are within specific ranges, and substantially has an Mw within a specific range, the acrylic acid-based copolymer is suitable as a major component of a water treatment agent that exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate. The acrylic acid-based copolymer of the present invention may also be used as a component of an agent that reduces or suppresses the formation of a scale due to a substance other than calcium phosphate, a dispersant for inorganic particles, a surfactant, an antistatic agent, a detergent composition, and the like.

The method for producing an acrylic acid-based copolymer (AA/ATBS-based polymer) of the present invention can reduce or suppress the production of an acrylic acid-based copolymer having a molecular weight of 70,000 or more.

The water treatment agent of the present invention exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate.

[BRIEF DESCRIPTION OF THE DRAWING]

[0008]

FIG. 1 is a schematic view illustrating a production apparatus used in connection with the present invention.

[EMBODIMENTS FOR CARRYING OUT THE INVENTION]

[0009]

The acrylic acid-based copolymer (AA/ATBS-based polymer) of the present invention includes a structural unit (x) derived from acrylic acid or a sodium salt thereof, and a structural unit (y) derived from 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof. In the acrylic acid-based copolymer, the contents of the structural unit (x) and the structural unit (y) are respectively 35% to 90% by mass and 10% to 65% by mass based on 100% by mass of a total content of the structural unit (x) and the structural unit (y). The acrylic acid-based copolymer has a weight average molecular weight (Mw) of 2,000 to 30,000, and includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more in an amount of 0.30% or less by mass based on a total amount of polymers.

[0010]

In the AA/ATBS-based polymer of the present invention, the structural unit (x) included in the polymer is at least one of a structural unit derived from acrylic acid and a structural unit derived from a sodium salt of acrylic acid, and the structural unit (y) included is at least one of a structural unit derived from 2-acrylamido-2-methylpropanesulfonic acid and a structural unit derived from a sodium salt of 2-acrylamido-2-methylpropanesulfonic acid. In particular, the polymer is preferably a polymer that has at least one structural unit (y) including $\text{-SO}_3\text{Na}$.

[0011]

A content ratio of the structural unit (x) and the structural unit (y) in the AA/ATBS-based polymer of the present invention is respectively 35% to 90% by mass and 10% to 65% by mass based on 100% by mass of a total content of the structural unit (x) and the structural unit (y) from a viewpoint of obtaining a high capability to prevent precipitation of calcium phosphate and is preferably 40% to 80% by mass and 20% to 60% by mass, and more preferably 45% to 75% by mass and 25% to 55% by mass.

[0012]

When the AA/ATBS-based polymer of the present invention includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more, a content thereof is 0.30% or less by mass, preferably 0.10% or less by mass, and more preferably 0.05% or less by mass based on a total amount of polymers.

[0013]

An Mw of the AA/ATBS-based polymer of the present invention is in a range from 2,000 to 30,000 from a viewpoint of obtaining a high capability to prevent precipitation of calcium phosphate and is preferably from 4,000 to 20,000. A polydispersity (M_w/M_n) that is a ratio of the Mw to a number average molecular weight (M_n) is 3.8 or less, preferably 3.5 or less, and more preferably 3.1 or less. The lower limit of the polydispersity is normally 2.0.

[0014]

A structure of the AA/ATBS-based polymer of the present invention is not particularly limited. The polymer is preferably a random copolymer.

The AA/ATBS-based polymer of the present invention may be obtained preferably by a continuous polymerization method using monomers including acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof.

[0015]

In the present invention, a method for producing an AA/ATBS-based polymer (hereinafter, referred to as “production method of the present invention”) has a process in which monomers including acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof are polymerized while continuously supplying the monomers to a reactor.

[0016]

A particularly preferred method for producing an AA/ATBS-based polymer of the present invention is a method in which a production apparatus having three reactors connected is used, monomers including acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof are polymerized in the presence of a polymerization initiator in a first reactor while continuously supplying the monomers to the reactor, a resulting reaction mixture (hereinafter, referred to as “reaction mixture (S1)”) is transferred from the first reactor to a second reactor that is connected to the first reactor, the monomers included in the reaction mixture (S1) in the second reactor are polymerized, the resulting reaction mixture (hereinafter, referred to as “reaction mixture (S2)”) is transferred from the second reactor to a third reactor that is connected to the second reactor, and the pH of the polymer-containing liquid is adjusted to 9 or less in the third reactor. It is possible to produce a homogenous AA/ATBS-based polymer that mainly includes an acrylic acid-based copolymer having an Mw of 2,000 to 30,000 while reducing or suppressing the production of a high-molecular-weight acrylic acid-based copolymer as a by-product, by continuously effecting the monomer polymerization process, the polymer transfer process, and the like using a continuous tank-type polymerization apparatus. Note that the production method of the present invention substantially produces an acrylic acid-based copolymer having an Mw of 2,000 to 30,000, or a precursor thereof, through the monomer polymerization that is continuously effected in the second reactor and the third reactor.

[0017]

An apparatus used in the production method of the present invention is not particularly limited. FIG. 1 is a schematic view illustrating a production apparatus that has three reactors. The production apparatus (100) illustrated in FIG. 1 has a first reactor (10) including a means that supplies a raw material (15), a stirring means, a temperature-adjusting means, a reflux condenser means, a discharge means, and the like, a second reactor (20) including a means that supplies a raw material (25), a stirring means, a temperature-adjusting means, a reflux condenser means, a discharge means, and the like, and a third reactor (30) including a means that supplies a pH-adjusting agent and the like (35), a stirring means, a temperature-adjusting means, a reflux condenser means, a discharge means, and the like.

[0018]

In the first reactor (10), monomers including acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof, are continuously supplied to the reactor and the monomers are polymerized in the presence of a polymerization initiator. It is preferable that the monomers include acrylic acid or 2-acrylamido-2-methylpropanesulfonic acid. This reaction system uses water as a polymerization medium, and may optionally use a chain transfer agent.

A content of the acrylic acid in the monomers supplied to the first reactor (10) is preferably in a range from 35% to 90% by mass, more preferably from 40% to 80% by mass, and further preferably from 45% to 75% by mass. The monomer concentration in the first reactor (10) is preferably in a range from 20% to 200% by mass, and more preferably from 50% to 150% by mass based on 100% by mass of the

polymerization medium.

When implementing the production method of the present invention, it is preferable to effect 90% or more of the polymerization reaction in the first reactor (10) from the viewpoint of obtaining a polymer having a narrow molecular weight distribution. Therefore, it is preferable to supply at least 90% by mass of the monomers to the first reactor (10). It is more preferable to supply 95% or more by mass of the monomers to the first reactor (10). Further, it is preferable to polymerize the monomers in the first reactor (10) under conditions whereby the polymerization conversion of the monomers is 90% or more.

[0019]

Examples of the polymerization initiator include hydrogen peroxide; a persulfate such as sodium persulfate, potassium persulfate and ammonium persulfate; an azo-based compound such as dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), dimethyl 2,2'-azobis(isobutyrate), 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine] n-hydrate, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] disulfate dihydrate and 1,1'-azobis(cyclohexane-1-carbonitrile); an organic peroxide such as benzoyl peroxide, lauroyl peroxide, peracetic acid, di-t-butyl peroxide and cumene hydroperoxide; and the like. The polymerization initiators may be used singly or in combination of two or more types thereof. In the present invention, a persulfate is preferably used.

The polymerization initiator is used in an amount preferably from 0.2 to 2.0 parts by mass and more preferably from 0.5 to 1.5 parts by mass based on 100 parts by mass of the monomers.

[0020]

Examples of the chain transfer agent include a thiol-based chain transfer agent such as mercaptoethanol, thioglycerol, thioglycolic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, thiomalic acid, octyl thioglycolate, octyl 3-mercaptopropionate, 2-mercaptoethanesulfonic acid, n-dodecylmercaptan, octylmercaptan and butyl thioglycolate; phosphorous acid; hypophosphorous acid and salts thereof (e.g., sodium hypophosphite and potassium hypophosphite); sulfurous acid; hydrogen sulfite, dithionous acid, metabisulfite and salts thereof (e.g., sodium hydrogen sulfite, potassium hydrogen sulfite, sodium dithionite, potassium dithionite, sodium metabisulfite, and potassium metabisulfite); and the like. The chain transfer agents may be used singly or in combination of two or more types thereof.

The chain transfer agent is used in an amount preferably from 1 to 20 parts by mass and more preferably from 3 to 10 parts by mass based on 100 parts by mass of the monomers.

[0021]

The polymerization temperature (i.e., the temperature of the reaction system) in the first reactor

(10) is appropriately selected taking account of types of polymerization initiator and the like. The temperature is preferably in a range from 60°C to 100°C and more preferably from 70°C to 90°C so that polymerization proceeds smoothly.

The production method of the present invention is designed so that the polymerization of the monomers that are continuously supplied is not completed in the first reactor (10), but is completed in the second reactor (20) or the third reactor (30). Therefore, a reaction mixture (S1) that is obtained in the first reactor (10) and is supplied to the second reactor (20) normally includes a resulting polymer, unreacted monomers, the polymerization initiator, and the like. A reaction mixture (S2) that is obtained in the second reactor (20) and is supplied to the third reactor (30) may include the polymer, unreacted monomers, the polymerization initiator, and the like.

The average residence time of the monomers in the first reactor (10) is preferably in a range from 30 to 300 minutes and more preferably from 50 to 200 minutes.

[0022]

Subsequently, the monomers that remain in the reaction mixture (S1) supplied from the first reactor (10) are polymerized in the second reactor (20). In the second reactor (20), only the monomers included in the reaction mixture (S1) may be polymerized or the monomers included in the reaction mixture (S1) may be polymerized together with monomers that are additionally supplied. The second reactor (20) may be charged with a polymerization initiator, a polymerization medium, and the like in advance.

The temperature of the reaction system in the second reactor (20) is preferably in a range from 60°C to 100°C and more preferably from 70°C to 90°C. The polymerization temperature in the second reactor (20) may be the same as or different from the polymerization temperature in the first reactor (10).

The average residence time of the monomers in the second reactor (20) is preferably in a range from 20 to 200 minutes and more preferably from 30 to 100 minutes so that polymerization is completed while a homogeneous polymer is formed.

[0023]

After that, the monomers that remain in the reaction mixture (S2) supplied from the second reactor (20) are polymerized in the third reactor (30) while neutralizing a precursor of the acrylic acid-based copolymer included in the reaction mixture (S2). Since the pH of the reaction mixture (S2) is normally within a range from 1.0 to 5.0, neutralization is normally effected using an alkaline aqueous solution prepared by dissolving an alkaline substance such as a hydroxide, a chloride, or a carbonate of an alkali metal (e.g., sodium and potassium); a hydroxide, a chloride, or a carbonate of an alkaline-earth metal (e.g., calcium and magnesium); ammonia; and an organic amine (e.g., monoethanolamine, diethanolamine, and triethanolamine) in water. The alkaline substances may be used singly or in combination of two or more types thereof.

The third reactor (30) may be charged with a polymerization medium and the like in advance.

[0024]

The pH of the polymer-containing liquid in the third reactor (30) is adjusted to 9 or less (preferably 3.0 to 8.0) using the alkaline aqueous solution.

An AA/ATBS-based polymer-containing liquid that substantially includes an acrylic acid-based copolymer having an Mw of 2,000 to 30,000 and preferably has a solid content of 30% to 50% by mass, can thus be obtained. When water is used as the polymerization medium, a polymer aqueous solution is obtained.

[0025]

The production method of the present invention can effect a polymerization reaction under conditions in which the sodium concentration is constant. Therefore, a change in polymerization rate and the like due to a change in sodium concentration rarely occur, and it is possible to obtain a homogeneous AA/ATBS-based polymer having an Mw of 2,000 to 30,000 while reducing or suppressing the production of a high-molecular-weight polymer having a molecular weight of more than 70,000.

[0026]

The acrylic acid-based copolymer of the present invention is suitable as a component of a water treatment agent that exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate, an agent that reduces or suppresses the formation of a scale due to a substance other than calcium phosphate, a dispersant for inorganic particles, a surfactant, an antistatic agent, a detergent composition, and the like.

[0027]

The water treatment agent of the present invention is a material including the AA/ATBS-based polymer of the present invention, and is normally a composition further including water. The type of AA/ATBS-based polymer is not particularly limited. The water treatment agent of the present invention may include only one type of AA/ATBS-based polymer, or may include two or more types of AA/ATBS-based polymers.

[0028]

A content ratio of the AA/ATBS-based polymer in the water treatment agent of the present invention is preferably in a range from 5% to 45% by mass and more preferably from 10% to 35% by mass since the water treatment agent exhibits a sufficient effect.

[0029]

The water treatment agent of the present invention may optionally include an additional scale inhibitor such as polyacrylic acid or a salt thereof, 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; a defoamer; and the like.

[0030]

The water treatment agent of the present invention is suitably applied to calcium phosphate that

easily adheres to a heating surface of a heat exchanger, a cooling water pipe, or the like. It is possible to reduce or suppress a decrease in heat exchange efficiency, pipe clogging or the like that may occur in a cooling water system, a boiler water system, a seawater desalination plant, and the like by utilizing the water treatment agent of the present invention.

[EXAMPLES]

[0031]

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

[0032]

1. Production of acrylic acid-based copolymer

In the following Examples, a production apparatus 100 in which three reactors (first reactor 10, second reactor 20, and third reactor 30) that were respectively equipped with a stirrer and a condenser were sequentially connected (see FIG. 1), was used.

[0033]

Example 1 (Production by continuous polymerization)

The first reactor (10), the second reactor (20), and the third reactor (30) were charged with 2,100 g of water, and maintained at a temperature of 75°C. A 60% acrylic acid aqueous solution (hereinafter, referred to as “60% AA”) (11.0 g/min), a 50% sodium 2-acrylamido-2-methylpropanesulfonate aqueous solution (hereinafter, referred to as “50% ATBSNa”) (9.0 g/min), a 15% sodium persulfate aqueous solution (hereinafter, referred to as “15% NPS”) (0.5 g/min), and a 30% sodium hypophosphite aqueous solution (hereinafter, referred to as “30% NHP”) (2.5 g/min), were supplied to the first reactor (10) while stirring to effect polymerization. The reaction mixture included in the first reactor (10) was transferred to the second reactor (20) at a rate of 23.0 g/min while supplying the raw material (15) to the first reactor (10) so that an amount of liquid in the first reactor (10) was 2,100 g. An average residence time of the reaction mixture in the first reactor (10) was set to 90 minutes. The reaction mixture included in the second reactor (20) was transferred to the third reactor (30) at a rate of 23.0 g/min while the reaction mixture was supplied to the second reactor (20) from the first reactor (10). Polymerization was continuously effected while stirring in the second reactor (20) while maintaining an amount of liquid in the second reactor (20) to be 2,100 g. An average residence time of the reaction mixture in the second reactor (20) was set to 90 minutes. Water and a 48% NaOH aqueous solution were supplied to the third reactor (30), and the reaction mixture was discharged and collected from the third reactor (30) while the reaction mixture having a pH of 4.0 was supplied to the third reactor (30) from the second reactor (20). Neutralization was continuously effected while stirring in the third reactor (30) while maintaining the amount of liquid in the third reactor (30) to be 2,100 g so that the pH of the reaction mixture was adjusted

to 7.0. When 24 hours had elapsed from the start of production, a reaction mixture obtained within 1 hour was collected and a polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E1) was obtained (see Table 1).

[0034]

The acrylic acid-based copolymer (E1) was subjected to gel permeation chromatography (GPC) under the conditions listed below. The acrylic acid-based copolymer (E1) had an Mw of 8,000 and a polydispersity (Mw/Mn) of 2.8. A content of an acrylic acid-based copolymer having a molecular weight of 70,000 or more in the acrylic acid-based copolymer (E1) (determined by molecular weight fraction calculations) was 0.02%.

(GPC measurement conditions)

Device: HLC-8020 system manufactured by Tosoh Corporation

Detection: RI

Column: G4000PW×1, G3000PW×1, and G2500PW×1 (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

[0035]

Example 2 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E2) was obtained in the same manner as those in Example 1 except that a 30% sodium hydrogen sulfite aqueous solution (hereinafter may be referred to as “30% NaHSO₃”) was used instead of 30% NHP (see Table 1).

The acrylic acid-based copolymer (E2) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0036]

Example 3 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E3) was obtained in the same manner as those in Example 1 except that the usage amounts of 60% AA and 50% ATBSNa were changed (see Table 1).

The acrylic acid-based copolymer (E3) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0037]

Example 4 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E4) was obtained in the same manner as those in Example 2 except that the usage amounts of 60% AA and 50% ATBSNa were changed (see Table 1).

The acrylic acid-based copolymer (E4) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0038]

Example 5 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E5) was obtained in the same manner as those in Example 1 except that the usage amounts of 60% AA and 50% ATBSNa were changed (see Table 1).

The acrylic acid-based copolymer (E5) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0039]

Example 6 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E6) was obtained in the same manner as those in Example 2 except that the usage amounts of 60% AA and 50% ATBSNa were changed (see Table 1).

The acrylic acid-based copolymer (E6) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0040]

Example 7 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E7) was obtained in the same manner as those in Example 1 except that the usage amount of 30% NHP was changed (see Table 1).

The acrylic acid-based copolymer (E7) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0041]

Example 8 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E8) was obtained in the same manner as those in Example 2 except that the usage amount of 30% NaHSO₃ was changed (see Table 1).

The acrylic acid-based copolymer (E8) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0042]

Example 9 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E9) was obtained in the same manner as those in Example 1 except that the usage amount of 30% NHP was changed (see Table 1).

The acrylic acid-based copolymer (E9) was then analyzed in the same manner as in Example 1.

The results are listed in Table 1.

[0043]

Example 10 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E10) was obtained in the same manner as those in Example 2 except that the usage amount of 30% NaHSO₃ was changed (see Table 1).

The acrylic acid-based copolymer (E10) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0044]

Example 11 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E11) was obtained in the same manner as those in Example 1 except using 50% ATBSNa (5.0 g/min) and 50% ATBS (5.0 g/min) in combination instead of 50% ATBSNa alone (see Table 1).

The acrylic acid-based copolymer (E11) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0045]

Example 12 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E12) was obtained in the same manner as those in Example 2 except using 50% ATBSNa (5.0 g/min) and 50% ATBS (5.0 g/min) in combination instead of 50% ATBSNa alone (see Table 1).

The acrylic acid-based copolymer (E12) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0046]

Example 13 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E13) was obtained in the same manner as those in Example 1 except using 50% ATBS (8.0 g/min) instead of 50% ATBSNa (see Table 1).

The acrylic acid-based copolymer (E13) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0047]

Example 14 (Production by continuous polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (E14) was obtained in the same manner as those in Example 2 except using 50% ATBS (8.0 g/min) instead of 50% ATBSNa (see Table 1).

The acrylic acid-based copolymer (E14) was then analyzed in the same manner as in Example 1. The results are listed in Table 1.

[0048]

Comparative Example 1 (Production by semi-batch polymerization)

A reactor equipped with a stirrer and a condenser was charged with 250 g of water, and maintained at a temperature of 75°C. A mixture including 470 g of 70%AA and 450 g of 50%ATBSNa, 25 g of 15%NPS, and 100 g of a 30% sodium hypophosphite aqueous solution were respectively supplied to the reactor while stirring over 3 hours to effect polymerization. After supplying the raw materials completely, the reaction system was aged at a temperature of 75°C for 1 hour while stirring. Water and a 48% NaOH aqueous solution were supplied to the reaction mixture having a pH of 3.9 to obtain a polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (C1).

The acrylic acid-based copolymer (C1) was then analyzed in the same manner as those in Example 1. The acrylic acid-based copolymer (C1) had an Mw of 11,000 and a polydispersity (Mw/Mn) of 3.8. A content of an acrylic acid-based copolymer having a molecular weight of 70,000 or more in the acrylic acid-based copolymer (C1) (determined by molecular weight fraction calculations) was 1.0%.

[0049]

Comparative Example 2 (Production by batch polymerization)

A polymer aqueous solution (pH: 7.0) having a solid content of 40% and including an acrylic acid-based copolymer (C2) was obtained in the same manner as those in Comparative Example 1 except using 30%NaHSO₃ instead of 30%NHP.

The acrylic acid-based copolymer (C2) was then analyzed in the same manner as those in Example 1. The acrylic acid-based copolymer (C2) had an Mw of 12,000 and a polydispersity (Mw/Mn) of 3.8. A content of an acrylic acid-based copolymer having a molecular weight of 70,000 or more in the acrylic acid-based copolymer (C2) (determined by molecular weight fraction calculations) was 1.0%.

[0050]

2. Evaluation of water treatment agent

The polymer aqueous solutions having a solid content of 40% and including an acrylic acid-based copolymer obtained in Examples 1 to 14 and Comparative Examples 1 and 2 were used as a water treatment agent, and the effect of reducing or suppressing the formation of a scale due to calcium phosphate was evaluated in the following method.

(Calcium phosphate scale reduction/suppression test)

An acrylic acid-based copolymer aqueous solution, disodium phosphate and calcium chloride were used to prepare a liquid having an acrylic acid-based copolymer concentration of 30 mg/L, a

disodium phosphate concentration of 90 mg/L, and a calcium chloride concentration of 375 mg/L in a volume of 180 mL. Subsequently 20 mL of a 0.21% sodium hydrogen carbonate aqueous solution was added while stirring the liquid and sodium hydroxide was used to adjust the pH of the resulting mixture of 8.5. After allowing the mixture to stand at a temperature of 60°C for 3 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.

[0051]

The scale reduction/suppression rate achieved by the water treatment agents respectively including the acrylic acid-based copolymers obtained in Comparative Examples 1 and 2 was 81%. On the other hand, the scale reduction/suppression rate achieved by the water treatment agents respectively including the acrylic acid-based copolymers obtained in Examples 1 to 14 was as high as 90% to 99% (see Table 1).

[0052]

TABLE 1

		Example													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
First reactor	60%AA (g/min)	11.0	11.0	16.0	16.0	7.0	7.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
	50%ATBSNa (g/min)	9.0	9.0	4.0	4.0	13.0	13.0	9.0	9.0	9.0	9.0	5.0	5.0	-	-
	50%ATBS (g/min)	-	-	-	-	-	-	-	-	-	-	4.0	4.0	8.0	8.0
	15%NPS (g/min)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	30%NHP (g/min)	2.5	-	2.5	-	2.5	-	4.5	-	1.5	-	2.5	-	2.5	-
	30%NaHSO ₃ (g/min)	-	2.5	-	2.5	-	2.5	-	6.0	-	1.5	-	2.5	-	2.5
	Temperature (°C)	75	75	75	75	75	75	75	75	75	75	75	75	75	75
Second reactor	Average residence time (min)	90	90	90	90	90	90	90	90	90	90	90	90	90	90
	ATBS content [†] in monomers (%)	38	38	16	16	58	58	38	38	38	38	39	39	38	38
	Temperature (°C)	75	75	75	75	75	75	75	75	75	75	75	75	75	75
	Average residence time (min)	90	90	90	90	90	90	90	90	90	90	90	90	90	90
	PH of reaction mixture	4.0	4.0	3.6	3.6	4.5	4.5	4.0	4.0	4.0	4.0	3.0	3.0	1.2	1.2
Third reactor	Temperature (°C)	75	75	75	75	75	75	75	75	75	75	75	75	75	75
	Average residence time (min)	90	90	90	90	90	90	90	90	90	90	90	90	90	90
	Acrylic acid-based copolymer	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	E13	E14
	Solid content (%)	40	40	40	40	40	40	40	40	40	40	40	40	40	40
	pH	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Mw	8,000	9,000	7,000	8,000	12,000	13,000	3,500	3,500	23,000	28,000	10,000	11,000	12,000	14,000
	Mw/Mn	2.8	2.9	2.9	3.0	3.2	3.2	2.4	2.4	3.4	3.5	3.3	3.4	3.7	3.8
Content of polymer having a molecular weight of 70,000 or more (%)		0.02	0.02	0.07	0.07	0.04	0.04	0.01	0.01	0.08	0.1	0.2	0.2	0.3	0.3
Calcium phosphate scale reduction/suppression rate (%)		99	99	94	94	96	96	94	94	93	93	91	91	90	90

[†] When ATBSNa was used, the ATBS content was calculated based on unneutralized ATBS instead of an Na salt.

[INDUSTRIAL APPLICABILITY]

[0053]

The acrylic acid-based copolymer of the present invention is suitable as a component of a water treatment agent that exhibits an excellent effect of reducing or suppressing the formation of a scale due to calcium phosphate, an agent that reduces or suppresses the formation of a scale due to a substance other than calcium phosphate, a dispersant for inorganic particles, a surfactant, an antistatic agent, a detergent composition, and the like.

The water treatment agent of the present invention is suitably applied to calcium phosphate that easily adheres to a heating surface of a heat exchanger, a coolant pipe, and the like.

CLAIMS

1. An acrylic acid-based copolymer comprising a structural unit (x) derived from acrylic acid or a sodium salt thereof, and a structural unit (y) derived from 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof, the acrylic acid-based copolymer comprising the structural unit (x) and the structural unit (y) in a ratio of 35% to 90% by mass and 10% to 65% by mass, respectively, based on 100% by mass of a total content of the structural unit (x) and the structural unit (y) in the acrylic acid-based copolymer,

wherein the acrylic acid-based copolymer has a weight average molecular weight (M_w) of 2,000 to 30,000, and includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more in an amount of 0.30% or less by mass based on a total amount of polymers.

2. The acrylic acid-based copolymer according to claim 1, having a polydispersity (M_w/M_n) of 3.5 or less, the polydispersity being a ratio of a weight average molecular weight (M_w) to a number average molecular weight (M_n) of the acrylic acid-based copolymer.

3. The acrylic acid-based copolymer according to claim 1 or 2, wherein the structural unit (x) is a structural unit derived from a sodium salt of acrylic acid, and the structural unit (y) is a structural unit derived from a sodium salt of 2-acrylamido-2-methylpropanesulfonic acid.

4. A method for producing the acrylic acid-based copolymer according to any one of claims 1 to 3, comprising polymerizing monomers while continuously supplying the monomers to a reactor, the monomers comprising acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof.

5. A method for producing the acrylic acid-based copolymer according to any one of claims 1 to 3, the method being implemented using a production apparatus in which three reactors are connected, and comprising polymerizing monomers in a first reactor in the presence of a polymerization initiator while continuously supplying the monomers to the first reactor, the monomers comprising acrylic acid or a sodium salt thereof, and 2-acrylamido-2-methylpropanesulfonic acid or a sodium salt thereof, transferring a reaction mixture from the first reactor to a second reactor that is connected to the first reactor, polymerizing the monomers included in the reaction mixture in the second reactor, transferring a reaction mixture from the second reactor to a third reactor that is connected to the second reactor, and adjusting a pH of a polymer containing liquid to 9 or less in the third reactor.

6. The method for producing an acrylic acid-based copolymer according to claim 5, wherein the polymerization initiator comprises a persulfate.

7. The method for producing an acrylic acid-based copolymer according to claim 5 or 6, wherein the pH of the polymer containing liquid is adjusted to a range from 3.0 to 8.0 in the third reactor.

8. A water treatment agent comprising the acrylic acid-based copolymer according to any one of claims 1 to 3.

9. The water treatment agent according to claim 8, wherein the acrylic acid-based copolymer has a weight average molecular weight (M_w) of 4,000 to 20,000, includes an acrylic acid-based copolymer having a molecular weight of 70,000 or more in a ratio of 0.05% or less by mass based on a total amount of polymers, and has a polydispersity (M_w/M_n) of 3.5 or less, the polydispersity being the ratio of a weight average molecular weight (M_w) to a number average molecular weight (M_n) of the acrylic acid-based copolymer.