

DESCRIPTION

WATER-SOLUBLE POLYMER COMPOSITION, PRODUCTION METHOD FOR WATER-SOLUBLE POLYMER COMPOSITION, AND APPLICATION FOR WATER-SOLUBLE POLYMER COMPOSITION

5 Technical Field

[0001] The teaching relates to a water-soluble polymer composition, and to a manufacturing method thereof and a use thereof. More specifically, the teaching relates to a water-soluble polymer composition useful as a dispersant and scale inhibitor, and to a manufacturing method thereof.

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Background Art

[0002] In plants and the like that use industrial water containing silica, silica scales are known to precipitate and adhere to heat exchangers, cooling pipes and the like, causing problems of reduced cooling efficiency and pipe clogging. An effective way of preventing scale precipitation is to make sure that the silica concentration of the cooling water does not exceed the solubility limit, but with such an operating method the water input and discharge amounts are increased. In recent years, calls for reducing the amounts of water used in cooling water systems and the like have become grater with a view to saving energy and reducing costs, and this means that the problems caused by silica scales have become more conspicuous because operations are often carried out under conditions of high concentration. Under these circumstances, there is demand for the development of scale control agents with strong silica scale inhibiting ability.

[0003] Scale control agents for preventing silica scale precipitation have already been proposed. Patent Literature 1 discloses a scale inhibitor containing an acrylamide polymer and an acrylic acid polymer. Patent Literature 2 describes a cooling water system scale inhibitor containing a polyethylene glycol with a specific molecular weight range together with a phosphonic acid or salt thereof and/or a carboxylic acid polymer with a molecular weight of not more than 100,000.

[0004] Patent Literature 3 to 5 describe scale inhibitors containing copolymers of (meth)acrylic acid with sulfonic acid group-containing monomers and substituted (meth)acrylamides. Patent Literature 6 discloses a scale inhibitor containing a water-soluble copolymer comprising (meth)acrylic acid and N-substituted (meth)acrylamide as constituent units, together with a water-soluble organic phosphonic acid and the like.

Citation List

[0005]

Patent Literature 1: Japanese Patent Application Publication No. S61-107998

Patent Literature 2: Japanese Patent Application Publication No. H02-31894

Patent Literature 3: Japanese Patent Application Publication No. H04-356580

5 Patent Literature 4: Japanese Patent Application Publication No. H09-136078

Patent Literature 5: Japanese Patent Application Publication No. 2007-117876

Patent Literature 6: Japanese Patent Application Publication No. H01-299700

Summary

10 Technical Problem

[0006] However, with the polyacrylamide or other acrylamide polymer described in Patent Literature 1 the effects are not always satisfactory when the silicic acid concentration of the water is high. In Patent Literature 2, the effects are not always stable because the polyethylene glycol is easily affected by other ions.

15 Moreover, the scale inhibitors described in Patent Literature 3 to 6 have not been able to satisfactorily suppress precipitation of silica scales. Another problem is that foaming is likely to occur in water systems to which these scale prevention agents have been added.

[0007] Thus, there has yet to be a scale inhibitor that has excellent silica scale inhibiting ability, is free from the problem of foaming, and is capable of controlling scale production even in
20 operations in which the cooling water system or the like has a high silica concentration.

In addition, silica is widely used industrially as a white pigment in the papermaking industry, as an abrasive for polishing semiconductor substrates and the like, and as a stabilizer for cosmetics or pharmaceuticals and the like. For these various applications, there is increasing demand for dispersion stabilizers with excellent dispersion stability that can maintain silica
25 dispersions with low viscosity over a long period of time.

[0008] It is an object of the teaching to provide a water-soluble polymer composition useful for solving these problems, and a manufacturing method thereof. Another object is to provide a scale inhibitor capable of stably providing excellent silica scale inhibiting ability without causing foaming during use, as well as a dispersant excellent in silica dispersion stability.

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Solution to Technical Problem

[0009] In light of these problems, the inventors perfected the teaching after discovering as a result of earnest research that a water-soluble polymer composition obtained by polymerizing a monomer composition containing a carboxyl group-containing unsaturated monomer and a

specific (meth)acrylamide derivative in the presence of a chain transfer agent containing a phosphorous acid compound or hypophosphorous acid compound has excellent silica scale inhibiting ability and silica dispersibility while having the property of resisting forming.

[0010] The teaching is as follows.

[1] A water-soluble polymer composition, comprising a water-soluble polymer including (A) 40 to 95 mass parts of a structural unit derived from a carboxyl group-containing unsaturated monomer, (B) 5 to 30 mass parts of a structural unit derived from a (meth)acrylamide derivative having a C₁₋₈ alkyl group, and (C) 0 to 35 mass parts of a structural unit derived from another monomer (with the total of (A) to (C) being 100 mass parts), and further including (D) a structural unit derived from one or two or more compounds selected from phosphorous acid compounds and hypophosphorous acid compounds, the water-soluble polymer composition having a free phosphorus compound content of not more than 2.0 mass%.

[2] The water-soluble polymer composition according to [1] above, the water-soluble polymer includes a structural unit derived from a sulfonic acid group-containing vinyl monomer as the (C) structural unit derived from another monomer.

[3] A scale inhibitor, which contains the water-soluble polymer composition according to [1] or [2] above.

[4] A dispersant, which contains the water-soluble polymer composition according to [1] or [2] above.

[5] A method for manufacturing a water-soluble polymer composition, the method comprising polymerizing a monomer composition formed of (A) 40 to 95 mass parts of a carboxyl group-containing unsaturated monomer, (B) 5 to 30 mass parts of a (meth)acrylamide derivative having a C₁₋₈ alkyl group and (C) 0 to 35 mass parts of another monomer (with the total of (A) to (C) being 100 mass parts) by using as a chain transfer agent (D) 1.5 to 8.0 mass parts of one or two or more compounds selected from phosphorous acid compounds and hypophosphorous acid compounds.

Advantageous Effects of Invention

[0011] The water-soluble polymer composition of the teaching has excellent silica adsorption capacity and silica dispersion stability in water. Consequently, a scale inhibitor containing this water-soluble polymer composition has an excellent inhibitory effect on silica scale production, and a silica dispersion with excellent long-term dispersion stability at low viscosities can be obtained with a dispersant containing this water-soluble polymer composition. Moreover, problems due to foaming and the like can also be avoided when the composition is used

industrially.

Description of Embodiments

[0012]

5 The present teachings will be explained in detail below. In this Description, "(meth)acrylic" means acrylic and/or methacrylic, and "(meth)acrylate" means acrylate and/or methacrylate. A "(meth)acryloyl group" means an acryloyl group and/or a methacryloyl group.

[0013] In addition to a water-soluble polymer and water as a medium, the water-soluble
10 polymer composition of the teaching contains unreacted substances including the initiator and chain transfer agent described below, as well as decomposition products of these and the like.

The water-soluble polymer comprises (A) 40 to 95 mass parts of a structural unit derived from a carboxyl group-containing unsaturated monomer, (B) 5 to 30 mass parts of a structural unit derived from a (meth)acrylamide derivative having a C₁₋₈ alkyl group, and (C) 0 to
15 35 mass parts of a structural unit derived from another monomer (with the total of (A) to (C) being 100 mass parts), and is also provided with (D) a structural unit derived from one or two or more compounds selected from the phosphorous acid compounds and hypophosphorous acid compounds. The monomer components constituting each of the structural units are explained in detail below.

20 [0014] <(A) Carboxyl group-containing unsaturated monomer>

A vinyl monomer having at least one carboxyl group in the molecule may be used as the (A) carboxyl group-containing unsaturated monomer.

Specific examples include carboxyl group-containing vinyl compounds such as (meth)acrylic acid, itaconic acid, maleic acid, fumaric acid, crotonic acid and 2-carboxyethyl
25 (meth)acrylate; unsaturated acid anhydrides such as maleic anhydride, itaconic anhydride and citraconic anhydride; half ester compounds of these unsaturated acid anhydrides with alkyl alcohols; and salts thereof, and one or two or more of these may be used. Examples of the salts include alkali metal salts with sodium, potassium and the like, alkali earth metal salts with calcium, magnesium and the like, ammonium salts, and organic amine salts of
30 monoethanolamine, triethanolamine and the like.

Of these, (meth)acrylic acid, maleic acid and maleic anhydride are preferred because they have good polymerizability and can confer sufficient hydrophilicity on the resulting polymer, and acrylic acid is more preferred.

[0015] The amount of the (A) carboxyl group-containing unsaturated monomer used is in the range of 40 to 95 mass parts, or preferably 60 to 92 mass parts, or more preferably 70 to 90 mass parts given 100 mass parts as the total (total amount of monomers used) including the (B) (meth)acrylamide derivative having a C₁₋₈ alkyl group and the (C) other monomer described below. When polymerization is performed using a monomer composition containing 40 to 95 mass parts of the carboxyl group-containing unsaturated monomer, a structural unit derived from this monomer is contained in the resulting water-soluble polymer in the amount of 40 to 95 mass parts.

If the amount of the carboxyl group-containing unsaturated monomer used is less than 40 mass parts, it may be impossible to ensure adequate water solubility. If it exceeds 95 mass parts, adsorbitivity to silica may be insufficient because it is not possible to ensure enough of the Component (B), and the silica scale inhibiting ability and silica dispersibility may be unsatisfactory as a result.

[0016] <(B) (Meth)acrylamide derivative having C₁₋₈ alkyl group>

The (B) (meth)acrylamide derivative having a C₁₋₈ alkyl group is a (meth)acrylamide substituted with an alkyl group, in which the carbon number of the alkyl group is 1 to 8. When there are two N-substituted alkyl groups, the carbon number of the alkyl group is the sum of the numbers of carbon atoms contained in each alkyl group.

As examples of the (B) (meth)acrylamide derivative having a C₁₋₈ alkyl group, specific compounds include N-monoalkyl substituted (meth)acrylamides such as methyl (meth)acrylamide, ethyl (meth)acrylamide, n-propyl (meth)acrylamide, isopropyl (meth)acrylamide, n-butyl (meth)acrylamide, isobutyl (meth)acrylamide, tert-butyl (meth)acrylamide, n-hexyl (meth)acrylamide, n-octyl (meth)acrylamide and 2-ethylhexyl (meth)acrylamide; and N-dialkyl substituted (meth)acrylamides such as dimethyl (meth)acrylamide, diethyl (meth)acrylamide and dibutyl (meth)acrylamide, and one or two or more of these may be used.

[0017] Adsorbitivity to silica is improved by introducing a structural unit derived from a (B) (meth)acrylamide derivative having a C₁₋₈ alkyl group into the water-soluble polymer.

Adsorbitivity to silica tends to be higher the greater the carbon number, but if the carbon number is too high the polymer may be insufficiently soluble in water. From this perspective, the carbon number of the alkyl group is preferably 3 to 8, or more preferably 4 to 8. An alkyl group with a branched structure is advantageous for reducing foaming during use, and tert-butyl (meth)acrylamide is desirable as a specific compound.

[0018] The amount of the (B) (meth)acrylamide derivative having a C₁₋₈ alkyl group used is in

the range of 5 to 30 mass parts, or preferably 8 to 25 mass parts, or more preferably 10 to 20 mass parts given 100 mass parts as a total of the monomers used. When polymerization is performed using a monomer composition containing 5 to 30 mass parts of the (meth)acrylamide derivative having a C₁₋₈ alkyl group, a structural unit derived from this monomer is contained in the resulting water-soluble polymer in the amount of 5 to 30 mass parts.

If the amount of the (meth)acrylamide derivative having a C₁₋₈ alkyl group used less than 5 mass parts, adsorbitivity to silica may be insufficient, and the silica scale inhibiting ability and silica dispersibility may be unsatisfactory. If it exceeds 30 mass parts, it may be impossible to ensure adequate water solubility, and the silica scale inhibiting ability and silica dispersibility may be unsatisfactory as a result.

[0019] <(C) Other monomer>

The water-soluble polymer of the teaching may have a structural unit derived from (C) another monomer other than (A) and (B) above to the extent that this does not detract from the effects of the teaching. This (C) other monomer is not particularly limited as long as it is a monomer that can be copolymerized with (A) and (B) above. Specific examples include vinyl monomers containing sulfonic acid groups, vinyl monomers containing hydroxyl groups, (meth)acrylic acid alkyl ester compounds, aromatic vinyl monomers, vinyl monomers containing amino groups, vinyl monomers containing amido groups, vinyl monomers containing polyoxyalkylene groups, vinyl monomers containing alkoxy groups, vinyl monomers containing cyano groups, vinyl cyanide monomers, vinyl ether monomers, vinyl ester monomers and conjugated dienes. One of these alone or a combination of two or more may be used.

Of these, a vinyl monomer containing a sulfonic acid group is preferred because it has good silica scale inhibiting ability and silica dispersibility, and is also excellent for suppressing foaming during use.

[0020] Examples of the vinyl monomers containing sulfonic acid groups include sulfonic acid group-containing vinyl compounds such as 2-acrylamido-2-methylpropanesulfonic acid, allylsulfonic acid, methallylsulfonic acid, vinylsulfonic acid, styrenesulfonic acid, 3-allyloxy-2-hydroxypropanesulfonic acid, allyloxybenzenesulfonic acid and methallyloxybenzenesulfonic acid and salts thereof, and one or two or more of these may be used. Of these, 2-acrylamido-2-methylpropanesulfonic acid and its salts are preferred for their excellent polymerizability. Examples of these salts are similar to those described for the (A) carboxyl group-containing unsaturated monomer.

[0021] Examples of the vinyl monomers containing hydroxyl groups include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethylene

glycol mono(meth)acrylate and N-methylol (meth)acrylamide, and one or two or more of these may be used.

[0022] Examples of the (meth)acrylic acid alkyl ester monomers include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, isoamyl (meth)acrylate, n-hexyl (meth)acrylate, 2-methylpentyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, n-octadecyl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate and benzyl (meth)acrylate. One of these alone or a combination of two or more may be used.

[0023] Examples of the aromatic vinyl monomers include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α -methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-tert-butylstyrene, tert-butoxystyrene, vinyl toluene, vinyl naphthalene, halogenated styrene, styrenesulfonic acid and α -methylstyrenesulfonic acid. One of these alone or a combination of two or more may be used.

[0024] Examples of the vinyl compounds containing amino groups include dimethylaminomethyl (meth)acrylate, diethylaminomethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-diethylaminoethyl (meth)acrylate, 2-(di-n-propylamino)ethyl (meth)acrylate, 2-dimethylaminopropyl (meth)acrylate, 2-diethylaminopropyl (meth)acrylate, 2-(di-n-propylamino)propyl (meth)acrylate, 3-dimethylaminopropyl (meth)acrylate, 3-diethylaminopropyl (meth)acrylate and 3-(di-n-propylamino)propyl (meth)acrylate. One of these alone or a combination of two or more may be used.

[0025] Examples of the vinyl compounds containing amido groups include (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide and N-methylol (meth)acrylamide. One of these alone or a combination of two or more may be used.

[0026] Examples of the vinyl compounds containing polyoxyalkylene groups include (meth)acrylic acid esters of alcohols having polyoxyethylene and/or polyoxypropylene groups. One of these alone or a combination of two or more may be used.

[0027] Examples of the vinyl compounds containing alkoxy groups include 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-(n-propoxy)ethyl (meth)acrylate, 2-(n-butoxy)ethyl (meth)acrylate, 3-methoxypropyl (meth)acrylate, 3-ethoxypropyl (meth)acrylate, 2-(n-propoxy)propyl (meth)acrylate and 2-(n-butoxy)propyl (meth)acrylate. One of these alone or a combination of two or more may be used.

[0028] Examples of (meth)acrylic acid ester compounds having cyano groups include

cyanomethyl (meth)acrylate, 1-cyanoethyl (meth)acrylate, 2-cyanoethyl (meth)acrylate, 1-cyanopropyl (meth)acrylate, 2-cyanopropyl (meth)acrylate, 3-cyanopropyl (meth)acrylate, 4-cyanobutyl (meth)acrylate, 6-cyanoethyl (meth)acrylate, 2-ethyl-6-cyanoethyl (meth)acrylate and 8-cyanoethyl (meth)acrylate. One of these alone or a combination of two or more may be used.

[0029] Examples of the vinyl cyanide compounds include acrylonitrile, methacrylonitrile and ethacrylonitrile. One of these alone or a combination of two or more may be used.

[0030] Examples of the vinyl ether compounds include vinyl methyl ether, vinyl ethyl ether, vinyl-n-butyl ether, vinyl phenyl ether and vinyl cyclohexyl ether. One of these alone or a combination of two or more may be used.

Examples of the vinyl ester compounds include vinyl formate, vinyl acetate and vinyl propionate. One of these alone or a combination of two or more may be used.

[0031] Examples of the conjugated dienes include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, 3-butyl-1,3-octadiene and chloroprene. One of these alone or a combination of two or more may be used.

[0032] Other examples include maleimide compounds such as maleimide, N-methylmaleimide, N-butylmaleimide, N-phenylmaleimide and N-cyclohexylmaleimide; maleic acid ester compounds; itaconic acid ester compounds; and N-vinyl heterocyclic compounds such as vinyl pyridine.

[0033] The amount of the (C) other monomer used is in the range of 0 to 35 mass parts or preferably 0 to 25 mass parts given 100 mass parts as the total of the monomers used. When polymerization is performed using a monomer composition containing 0 to 35 mass parts of this other monomer, a structural unit derived from this monomer is contained in the resulting water-soluble polymer in the amount of 0 to 35 mass parts.

[0034] <(D) Phosphorous acid compound and hypophosphorous acid compound>

One or two or more compounds selected from phosphorous acid and its salts and hypophosphorous acid and its salts can be used as the (D) phosphorous acid compound and hypophosphorous acid compound. Examples of phosphite salts and hypophosphite salts include sodium salts (e.g., sodium hypophosphite, disodium hydrogenphosphite (the same applies hereafter), potassium salts, lithium salts, calcium salts, magnesium salts and barium salts. Of these, the sodium salts are preferred for efficiently producing a low-molecular-weight water-soluble polymer and a highly transparent aqueous polymer solution, and sodium hypophosphite is especially desirable.

[0035] The phosphorous acid compound and hypophosphorous acid compound can be applied as chain transfer agents. Thus, by performing polymerization in the presence of these compounds, it is possible to introduce structural units derived from the phosphorous acid compound and hypophosphorous acid compound into the resulting polymer. In the water-soluble polymer composition of the teaching, performance such as silica dispersibility is enhanced and the effect of suppressing foaming during use is obtained because a structural unit derived from a phosphorous acid compound and hypophosphorous acid compound has been introduced into the water-soluble polymer contained in the composition.

[0036] When polymerization is performed in the presence of a phosphorous acid compound or hypophosphorous acid compound, part of these is not introduced into the polymer and remains in the system as unreacted material. The performance of the water-soluble polymer composition as a scale inhibitor and dispersant may be adversely affected by free phosphorus compounds including this residual unreacted material and phosphoric acid compounds produced by oxidation of these. Consequently, in the teaching the amount of these free phosphorus compounds contained in the polymer composition may be necessary not more than 2.0 mass%, and is preferably not more than 1.6 mass% or more preferably not more than 1.2 mass% of the total amount of the polymer composition. The content of the free phosphorus compounds can be determined by ^{31}P -NMR measurement as described in the examples below.

[0037] In the teaching, the molecular weight of the water-soluble polymer can be adjusted by adjusting the amounts of the chain transfer agents including phosphorous acid compounds and hypophosphorous acid compounds.

The weight-average molecular weight (M_w) of the water-soluble polymer of the teaching is preferably 3,000 to 20,000, or more preferably 3,000 to 15,000, or still more preferably 5,000 to 15,000 from the standpoint of silica scale inhibiting ability and silica dispersibility. When the weight-average molecular weight is at least 3,000 adsorbitivity to silica is improved, while when it is not more than 20,000 dispersion stability is improved. The weight-average molecular weight can be measured by gel permeation chromatography (GPC) using a standard substance such as sodium polyacrylate.

[0038] <Method of manufacturing water-soluble polymer composition>

The manufacturing method of the teaching is provided with a polymerization step in which in an aqueous medium 40 to 95 mass parts of a (A) carboxyl group-containing unsaturated monomer, 5 to 30 mass parts of a (B) (meth)acrylamide derivative having a C_{1-8} alkyl group and 0 to 35 mass parts of (C) another monomer (with the total of (A) to (C) being 100 mass parts) are polymerized. The polymerization may be performed using 1.5 to 8.0 mass parts of one or two or

more compounds selected from the phosphorous acid compounds and hypophosphorous acid compounds as a chain transfer agent.

[0039] As discussed above, the amount of the phosphorous acid compound and

hypophosphorous acid compound used is preferably in the range of 1.5 to 8.0 mass parts given

100 mass parts as the total of the monomers used. The amount of the phosphorous acid

compound and hypophosphorous acid compound used is more preferably in the range of 2.0 to

7.0 mass parts, or still more preferably in the range of 2.5 to 6.0 mass parts. By performing

polymerization using a monomer composition containing 1.5 to 8.0 mass parts of a phosphorous acid compound and hypophosphorous acid compound, it is possible to introduce a structural unit

10 derived from these compounds into the resulting water-soluble polymer, and easily obtain a molecular weight suited to a scale inhibitor and dispersant.

If at least 1.5 mass parts of the phosphorous acid compound and hypophosphorous acid compound are used, a satisfactory foaming suppression effect can be obtained due to the use. If

the amount is not more than 8.0 mass parts, it is easy to keep the content of free phosphorus

15 compounds in the water-soluble polymer composition to not more than 2.0 mass parts, and avoid adverse effects on dispersibility and other performance.

[0040] The method of polymerizing the water-soluble polymer is not particularly limited, but is preferably a solution polymerization method. With solution polymerization, it is possible to obtain the target water-soluble polymer composition as a uniform solution.

20 [0041] Apart from the phosphorous acid compound and hypophosphorous acid compound, a known chain transfer agent such as sodium bisulfite, mercaptoacetic acid, mercaptopropionic acid, 2-propanethiol, 2-mercaptoethanol or thiophenol may also be included.

[0042] The method for adding the phosphorous acid compound and hypophosphorous acid compound is not particularly limited. In the case of a batch or semi-batch process, the total

25 amount of the phosphorous acid compound and hypophosphorous acid compound may be input into the reactor before polymerization, or the total amount may be input during polymerization.

Alternatively, a part may be input into the reactor before polymerization, and the remainder input during polymerization. Each input may be performed all at once, or intermittently in multiple additions. Part or all of the amount may also be input continuously. Of these methods, inputting

30 a part into the reactor before polymerization and then inputting the remainder continuously during polymerization is desirable because it allows for efficient introduction of a structural unit derived from the phosphorous acid compound and hypophosphorous acid compound into the polymer, and makes it easier to obtain a polymer with a relatively narrow molecular weight distribution. The amount of the phosphorous acid compound and hypophosphorous acid

compound added to the reactor before polymerization is preferably in the range of 5 to 40 mass%, or more preferably 10 to 25 mass% of the total amount of the phosphorous acid compound and hypophosphorous acid compound used in order to obtain a polymer with a relatively narrow molecular weight distribution.

5 [0043] A polymerization initiator is usually used in the polymerization step. The polymerization initiator is not particularly limited, and a known polymerization initiator may be used, but a radical polymerization initiator is preferred.

Examples of the radical polymerization initiator include hydrogen peroxide; persulfate salts such as sodium persulfate, potassium persulfate and ammonium persulfate; organic
10 peroxides such as peracetic acid, t-butyl hydroperoxide, cumene hydroperoxide, di-t-butyl peroxide and t-butyl cumyl peroxide; and azo compounds such as 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine] hydrate, 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis[2-(2-imidazoline-2-yl)propane] dihydrochloride and 2,2'-azobis[2-(2-imidazoline-2-yl)propane] disulfate
15 dihydrate.

One of these radical polymerization initiators alone or a combination of two or more may be used. Of those listed above, the persulfate salts and azo compounds are preferred for ease of controlling the polymerization reaction, and the persulfate salts are particularly preferred.

[0044] The polymerization initiator is diluted with an aqueous medium for example, and
20 supplied to the reactor through a separate supply port from the monomers.

The ratio of the polymerization initiator used is not particularly limited, but is preferably 0.1 to 15 mass%, or especially 0.5 to 10 mass% based on the total weight of all the monomers constituting the water-soluble polymer. The polymerization efficiency can be improved by making this ratio at least 0.1 mass%, while if it is not more than 15 mass%, the stability of the
25 resulting polymer may be improved and excellent performance may be obtained when it is used as a dispersant or the like.

In some cases, the polymer may also be manufactured using a water-soluble redox polymerization initiator as the polymerization initiator. Examples of the redox polymerization initiator include combinations of oxidants (such as the peroxides listed above) with reducing
30 agents such as sodium bisulfite, ammonium bisulfite, sodium sulfite and sodium hydrosulfite, or with iron alum and potassium alum.

[0045] The reaction temperature for polymerization is selected appropriately according to the types of polymerization initiator and monomers and the like, but is normally at least 60°C, or preferably at least 65°C, or more preferably at least 70°C. The upper limit of the polymerization

temperature is the boiling point of the reaction solution, which is normally about 110°C. In order to avoid decomposition and denaturation and the like of the raw materials due to heating, it is preferably not more than 100°C, or more preferably not more than 95°C, or still more preferably not more than 90°C.

5 The polymerization method may be a batch polymerization method or a continuous polymerization method. In the case of a batch polymerization method, the time required by the step of supplying the raw material (raw material composition) containing the monomers and the like is preferably 2 to 12 hours, or more preferably 3 to 8 hours. If the required time is at least 2 hours it is easy to remove the heat of polymerization, while if it is not more than 12 hours
10 productivity is increased, which are preferable.

 In the case of continuous polymerization, the process preferably uses a multistage CSTR (a continuous stirred tank reactor having multiple reaction tanks). In this case, the average residence time in each reaction tank is preferably 60 to 240 minutes, or more preferably 80 to 180 minutes. If the average residence time is at least 60 minutes, the amount of unreacted
15 monomers can be reduced. If it is not more than 240 minutes, the size of the reaction tanks can be smaller.

[0046] The amount of the monomers used in the polymerization reaction is not particularly limited, but is normally in the range of 10 to 70 mass%, or preferably 20 to 60 mass%, or more preferably 30 to 50 mass% of the total amount of the reaction solution.

20 The concentration of the water-soluble polymer contained in the aqueous solution obtained from the polymerization reaction is preferably in the range of 10 to 70 mass%, or more preferably 20 to 60 mass%, or still more preferably 30 to 50 mass%.

[0047] Following this polymerization step, the manufacturing method of the teaching may also be provided with a neutralization step in which the pH of the resulting water-soluble polymer
25 composition is adjusted to a desired pH. In the neutralization step, the pH of the composition may be adjusted by using an alkali agent to neutralize the acidic groups in the water-soluble polymer. For the alkali agent, hydroxides or carbonates of alkali metals such as sodium and potassium; hydroxides of alkali earth metals such as calcium and magnesium; ammonia; and organic amines such as monoethanolamine, diethanolamine and triethanolamine can be used as
30 is, or as aqueous solutions dissolved in water.

 In the teaching, the pH of the water-soluble polymer composition is preferably 0 to 10, or more preferably 1 to 8, or still more preferably 2 to 6.

[0048] In addition to the polymerization step and neutralization step, the manufacturing method of the teaching may also be provided with a concentration adjustment step in which the

concentration of the polymer composition is adjusted. A medium such as water can be added in the concentration adjustment step to dilute the water-soluble polymer composition and thereby adjust the concentration, viscosity and the like of the composition. The water-soluble polymer composition can also be concentrated in the concentration adjustment step by removing a part of the medium under conditions such as heating or reduced pressure as necessary.

[0049] <Scale inhibitor>

The water-soluble polymer composition of the teaching is suitable as a water treatment agent, and may be used as a water treatment agent in its original form as an aqueous solution. It may also contain another scale inhibitor as necessary.

Examples of other scale inhibitors include poly(meth)acrylic acid or its salts, polymaleic acid or its salts, (meth)acrylic acid copolymers, styrene/maleic acid copolymers and maleic acid/sulfonic acid group-containing monomer copolymers.

[0050] In addition, the scale inhibitor of the teaching may also be made into a water treatment agent by compounding other components such as corrosion inhibitors, slime prevention agents, bactericides, antifoaming agents and organic solvents to the extent that these do not detract from the effects of the teaching.

Examples of corrosion inhibitors include amines such as cyclohexylamine, diethanolamine and octadecylamine; and azoles such as benzotriazole and tolyltriazole.

Examples of slime prevention agents include quaternary ammonium salts such as alkyl dimethylbenzyl ammonium chloride, and methylisothiazoline, chloromethylisothiazoline and chloromethyltrithiazoline.

[0051] A water treatment agent containing the scale inhibitor of the teaching can be used to control problems such as reduced heat exchange efficiency and pipe clogging in cooling water systems, boiler water systems and seawater desalination systems.

The amount of the scale inhibitor used is set at the time of use depending on various factors such as the water to be treated and the operating conditions. The concentration of the water-soluble polymer of the teaching in the water treatment system is normally 1 to 1,000 ppm, or preferably 5 to 500 ppm.

[0052] <Dispersant>

The pH and solids concentration of the dispersant of the teaching are not particularly limited. The pH is preferably 0 to 10, or more preferably 1 to 8, or still more preferably 2 to 6. The solids concentration is preferably 10 to 70 mass%, or more preferably 26 to 60 mass%, or still more preferably 30 to 50 mass%.

[0053] The dispersant of the teaching may also contain other components such as an

antifoaming agent and preservative.

Examples of the antifoaming agent include polyether systems, mineral oil systems, silicone systems and amide systems. When the dispersant of the teaching contains such an antifoaming agent, the content thereof is preferably 0.01 to 1.0 mass parts per 100 mass parts of the acrylic polymer.

[0054] Examples of the preservative include isothiazoline preservatives and paraben. When the dispersant of the teaching contains such a preservative, the content thereof is preferably 0.001 to 1.0 mass parts per 100 mass parts of the acrylic polymer.

[0055] The amount of the dispersant of the teaching that is used is not particularly limited, but is preferably adjusted so that the water-soluble polymer of the teaching constitutes 0.1 to 10.0 mass parts and the aqueous medium constitutes 20 to 500 mass parts per 100 mass parts of the silica or other dispersoid. Together with the dispersant of the present teaching, another dispersant may be used.

The dispersant may be added all at once, or in two or more batches. It may also be added continuously. A method of adding in batches or a method of continuous addition is especially desirable for obtaining a dispersion with low viscosity.

[Examples]

[0056] The teaching is explained in detail below based on examples. In the explanations below "parts" are mass parts, and "%" means mass%.

The molecular weights of the water-soluble polymers obtained in each example and their solids concentrations in aqueous solution were measured by the methods described below.

[0057] <Molecular weight measurement (GPC)>

The weight-average molecular weight (Mw) and number-average molecular weight (Mn) of the polymer were measured by gel permeation chromatography (GPC).

An HLC8020 system (Tosoh Corporation) was used as the GPC equipment, using G4000PWx1, G3000PWx1 and G2500PWx1 columns (all Tosoh Corporation) connected in a sequence. 0.1 MNaCl + phosphoric acid buffer (pH 7) was used as the eluent, and a calibration curve was prepared using polyacrylic acid Na (Sowa Science Corporation).

[0058] <Solid content>

About 1 g of the measurement sample was weighed (a) and then dried for 30 minutes in a ventilating drier at 155°C, the residue was measured (b), and the solid content was calculated by the following formula. A weighing bin was used for measurement. The other operations conformed to JIS K 0067-1992 (Test Methods for Loss and Residue of Chemical Products).

$$\text{Solid content (\%)} = (b/a) \times 100$$

[0059] Example 1

<Manufacture of water-soluble polymer composition E1>

650 g of water and 17 g of a 30% sodium hypophosphite aqueous solution were loaded into a flask equipped with a stirrer and a condenser, and maintained at 80°C. A mixture of 1,025 g of an 80% acrylic acid aqueous solution (hereunder also called "80% AA") with 180 g of tert-butyl acrylamide (hereunder also called "TBAM"), 83 g of a 30% sodium hypophosphite aqueous solution, and 83 g of a 30% sodium persulfate aqueous solution were each supplied continuously to the flask over the course of 4 hours, and a polymerization reaction was performed. After all the materials had been supplied, the reaction solution was maintained and reacted for a further 1 hour at 80°C. The reaction solution was maintained at 80°C as a 48% sodium hydroxide aqueous solution and deionized water were supplied, to obtain an aqueous solution with a solids concentration of 40% and a pH of 3.0 containing a water-soluble polymer E1 (water-soluble polymer composition E1).

The weight-average molecular weight (Mw) of the water-soluble polymer E1 as measured by gel permeation chromatography (GPC) was 10,000.

The content of free phosphorus compounds (phosphoric acid compounds, phosphorous acid compounds and hypophosphorous acid compounds) in the water-soluble polymer composition E1 was measured by ^{31}P -NMR. For the NMR measurement conditions, a JNM-ECA400 (JEOL Ltd.) was used, and heavy water was used as the medium. Peaks were obtained near 8.0 ppm for hypophosphorous acid, near 3.0 ppm for phosphorous acid and near 0 ppm for phosphoric acid, and the amount of free phosphorus compounds contained in the water-soluble polymer composition E1 was calculated to be 0.5%.

[0060] The water-soluble polymer composition E1 obtained above was evaluated as a scale inhibitor and dispersant.

<Silica precipitation suppression test>

Sodium metasilicate nonahydrate, magnesium sulfate heptahydrate, the water-soluble polymer composition E1 and sodium hydrogencarbonate were added to ion-exchange water, and the Si concentration was adjusted to 200 mg SiO_2/L , the Mg concentration corresponding to 100mg/L of CaCO_3 , the E1 concentration to 100 mg solid/L and the carbonate ion concentration corresponding to 500 mg /L of CaCO_3 . The pH was adjusted to 9.0 with a 1% aqueous sulfuric acid solution, the mixture was left standing for 3 days at 25°C, and the resulting precipitate was filtered out with a 0.1 μm membrane filter to obtain a filtrate "SE1".

Separately, sodium metasilicate nonahydrate, magnesium sulfate heptahydrate and sodium hydrogencarbonate were added to ion-exchange water, and the Si concentration was

adjusted to 200 mg SiO₂/L, the Mg concentration corresponding to 100 mg /L of CaCO₃ and the carbonate ion concentration corresponding to 500 mg /L of CaCO₃. The pH was adjusted to 9.0 with a 1% aqueous sulfuric acid solution, the mixture was left standing for 3 days at 25°C, and the resulting precipitate was filtered out with a 0.1 μm membrane filter to obtain a filtrate "SB".

The value of (silica concentration in "SE1"/silica concentration in "SB") was calculated as "1.28" from the silica concentrations of "SE1" and "SB" according to the molybdenum yellow method, and taken as a measure of the silica precipitation suppression ability of the water-soluble polymer composition E1. The higher this number, the greater the silica precipitation suppression ability.

[0061] <Silica dispersibility test>

2.4 g of the water-soluble polymer composition E1 with a solids concentration of 40%, 588 g of ion-exchange water and 240 g of silica powder (Tosoh Silica Corporation, Nipsil HD-2 (product name)) were placed in a cylindrical container, and stirred for 10 minutes at 4,000 rpm to prepare a dispersed slurry. The viscosity of this slurry on the day of dispersion was 160 mPa·s as measured under conditions of 25°C, 60 rpm with a B-type viscometer. After the slurry had been left standing for 7 days at 25°C, the viscosity was 240 mPa·s.

[0062] <Foaming resistance test>

10 g of the water-soluble polymer composition E1 with a solids concentration of 40% and 390 g of ion-exchange water were loaded into a cylindrical container, and stirred for 15 seconds at 1,400 rpm. When the presence or absence of foaming was evaluated with the naked eye by observing the external appearance of the test liquid 60 seconds after stirring had stopped, no foaming was observed.

[0063] Examples 2 to 11, Comparative Examples 1 to 4

The same operations were performed as in Example 1 except that types and amounts of the raw materials during polymerization were as shown in Tables 1 and 2, to obtain water-soluble polymer compositions E2 to E11 and C1 to C4 with solids concentrations of 40%. The weight-average molecular weights of the polymers, the pH values of their 40% aqueous solutions and their properties as scale inhibitors and dispersants were evaluated as in Example 1, with the results shown in Tables 1 and 2.

[0064]

[Table 1]

Water-soluble polymer		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Initial input raw material	Water	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
	30% NHP	650	650	800	650	650	650	650	650	650	650	650
	30% Na ₂ HPO ₃	17	-	17	20	33	33	33	33	33	10	50
	30% sodium bisulfite	-	33	-	-	-	-	-	-	-	-	-
	Maleic anhydride	-	-	120	13	-	-	-	-	-	-	-
	48% NaOH	-	-	50	-	-	-	-	-	-	-	-
Continuously supplied raw material	80% AA	1025	1063	950	950	950	950	950	1000	763	950	950
	TBAM	180	150	120	120	120	-	-	80	270	120	120
	NIPAM	-	-	-	-	-	120	-	-	-	-	-
	DEAA	-	-	-	-	-	-	120	-	-	-	-
	ATBS	-	-	-	120	120	120	120	120	120	120	120
	30% NHP	83	-	83	83	133	133	133	133	133	50	200
	30% Na ₂ HPO ₃	-	133	-	-	-	-	-	-	-	-	-
	30% sodium bisulfite	-	-	-	50	-	-	-	-	-	-	-
Polymer composition	30% NPS	83	83	67	67	67	67	67	67	67	67	67
	Component (A)	82	85	88	76	76	76	76	80	61	76	76
	Component (B)	18	15	12	12	12	12	12	8	27	12	12
	Component (C)	0	0	0	12	12	12	12	12	12	12	12
	Component (D)	3.0	5.0	3.0	3.1	5.0	5.0	5.0	5.0	5.0	1.8	7.5
	Solids content (%)	40	40	40	40	40	40	40	40	40	40	40
Product	PH	3.0	4.0	4.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Mw	10000	14000	8000	10000	9000	9000	10000	10000	7000	17000	5000
	Free phosphorus compound concentration (%)	0.5	1.0	0.5	0.5	0.9	0.9	0.9	0.9	0.9	0.2	1.5
	Silica precipitation suppression ability (times)	1.28	1.26	1.28	1.28	1.28	1.24	1.23	1.21	1.26	1.24	1.27
Silica precipitation suppression test	Slurry viscosity (same day) (mPa·s)	160	170	170	160	150	180	180	180	200	230	170
	Slurry viscosity (7th day) (mPa·s)	240	250	250	230	220	260	260	250	310	280	320
Foaming test	Foaming after 60 seconds of stirring	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming	No foaming

[0065]

[Table 2]

Water-soluble polymer		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Initial input raw material	Water	C1 650	C2 650	C3 650	C4 650
	30% NHP	33	33	-	67
	30% Na ₂ HPO ₃	-	-	-	-
	30% sodium bisulfite	-	-	33	-
	Maleic anhydride	-	-	-	-
	48% NaOH	-	-	-	-
	80% AA	1100	663	950	950
Continuously supplied raw material	TBAM	-	350	120	120
	NIPAM	-	-	-	-
	DEAA	-	-	-	-
	ATBS	120	120	120	120
	30% NHP	133	133	-	267
	30% Na ₂ HPO ₃	-	-	-	-
	30% sodium bisulfite	-	-	133	-
Polymer composition	30% NPS	67	67	67	67
	Component (A)	88	53	76	76
	Component (B)	0	35	12	12
	Component (C)	12	12	12	12
	Component (D)	5.0	5.0	0.0	10.0
Product	Solids content	40	40	40	40
	PH	3.0	3.0	3.0	3.0
	Mw	11000	6000	10000	4000
	Free phosphorus compound concentration	0.9	0.9	0.0	2.4
	Silica precipitation suppression ability	1.11	1.21	1.19	1.21
Silica dispersibility test	Slurry viscosity (same day)	260	320	330	220
	Slurry viscosity (7th day)	380	610	490	690
Foaming test	Foaming after 60 seconds of stirring	No foaming	Much foaming	Much foaming	No foaming

[0066] The details of the compounds shown in Tables 1 and 2 are as follows.

30% NHP: 30% sodium hypophosphite aqueous solution

30% Na_2HPO_3 : 30% solution of disodium hydrogen phosphite pentahydrate

5 48% NaOH: 48% sodium hydroxide aqueous solution

80% AA: 80% acrylic acid aqueous solution

TBAM: tert-butyl acrylamide

NIPAM: N-isopropylacrylamide

DEAA: Diethylacrylamide

10 ATBS: 2-acrylamido-2-methylpropanesulfonic acid

30% NPS: 30% sodium persulfate aqueous solution

Component (A): Carboxyl group-containing unsaturated monomer

Component (B): (Meth)acrylamide derivative having C_{1-8} alkyl group

Component (C): Other monomer

15 Component (D): Phosphorous acid compound and hypophosphorous acid compound

[0067] Examples 1 to 11, which are all experimental examples of the water-soluble polymer of the teaching, all exhibited excellent silica precipitation suppression ability and silica dispersibility, with no foaming during use. Looking at the amount of the (meth)acrylamide derivative having a C_{1-8} alkyl group (Component (B)), Examples 1 to 7 and 9 to 11 using at least 20 10 mass parts of the Component (B) exhibited better silica precipitation suppression than Example 8, which used less of the Component (B). Looking at the type of the Component (B), moreover, the silica precipitation suppression was greater in Examples 3 to 5 using the same amount of tert-butylacrylamide than in Example 6 using N-isopropylacrylamide and Example 7 using diethylacrylamide.

25 [0068] By contrast, in Comparative Example 1, in which the water-soluble polymer lacked a structural unit derived from the Component (B), poor results were obtained for silica precipitation suppression and silica dispersibility. In Comparative Example 2, in which the water-soluble polymer had more structural units derived from the Component (B), and Comparative Example 3, in which the water-soluble polymer lacked a structural unit derived 30 from the Component (D), the results showed that silica dispersibility was poor and there was much foaming during use, which would impede actual application. In Comparative Example 4, in which the content of free phosphorus compounds was high, foaming was not a problem but the silica dispersibility was unsatisfactory.

Industrial Applicability

[0069] The water-soluble polymer composition of the teaching has excellent adsorptivity to silica and silica dispersion stability in water. Therefore, a scale inhibitor containing the water-soluble polymer composition can be used as a water treatment agent to control problems such as

5 reduced heat exchange efficiency and pipe clogging in cooling water systems, boiler water systems and seawater desalination systems. Moreover, the water-soluble polymer composition of the teaching is also useful as a dispersant in cosmetics, abrasives and the like containing silica.

Claims

1. A water-soluble polymer composition, comprising a water-soluble polymer including (A) 40 to 95 mass parts of a structural unit derived from a carboxyl group-containing unsaturated monomer, (B) 5 to 30 mass parts of a structural unit derived from a (meth)acrylamide derivative having a C₁₋₈ alkyl group, and (C) 0 to 35 mass parts of a structural unit derived from another monomer (with the total of (A) to (C) being 100 mass parts), and further including (D) a structural unit derived from one or two or more compounds selected from phosphorous acid compounds and hypophosphorous acid compounds, the water-soluble polymer composition having a free phosphorus compound content of not more than 2.0 mass%.
5
- 10 2. The water-soluble polymer composition according to claim 1, wherein the water-soluble polymer includes a structural unit derived from a sulfonic acid group-containing vinyl monomer as the (C) structural unit derived from another monomer.
3. A scale inhibitor, which contains the water-soluble polymer composition according to claim 1 or 2.
- 15 4. A dispersant, which contains the water-soluble polymer composition according to claim 1 or 2.
- 20 5. A method of manufacturing a water-soluble polymer composition, the method comprising polymerizing a monomer composition formed of (A) 40 to 95 mass parts of a carboxyl group-containing unsaturated monomer, (B) 5 to 30 mass parts of a (meth)acrylamide derivative having a C₁₋₈ alkyl group and (C) 0 to 35 mass parts of another monomer (with the total of (A) to (C) being 100 mass parts) by using as a chain transfer agent (D) 1.5 to 8.0 mass parts of one or two or more compounds selected from phosphorous acid compounds and hypophosphorous acid compounds.