

SPECIFICATION

DISPERSANT FOR CALCIUM CARBONATE, AND PROCESS FOR CONTINUOUS PRODUCTION OF THE DISPERSANT

[FIELD OF THE INVENTION]

[0001]

The present invention relates to a dispersant for calcium carbonate and a continuous production method thereof. More specifically, the present invention relates to a dispersant for calcium carbonate, which leads to a calcium carbonate slurry having a reduced initial viscosity by wet grinding and prevents a significant increase in viscosity of the slurry with passage of time, and a continuous production method thereof.

[BACKGROUND ART]

[0002]

A calcium carbonate slurry obtained by wet grinding of calcium carbonate has been widely used as a paper coating agent, a paint pigment, and the like. When the slurry of calcium carbonate is produced, a dispersant for calcium carbonate is used in order to decrease the viscosity of the resulting calcium carbonate slurry.

A dispersant containing an acryl-based polymer is used as the dispersant for calcium carbonate in order to obtain a slurry having low viscosity.

Patent Literature 1 discloses a method for producing a dispersant wherein a polymer having a low molecular weight is produced using water as a solvent, and using a large amount of a chain transfer agent such as sodium hypophosphite. However, a calcium carbonate slurry prepared using a dispersant obtained by this method exhibits high viscosity, and may show a significant increase in viscosity with passage of time.

As a method without using a chain transfer agent such as sodium hypophosphite, Patent Literature 2 discloses a method wherein a dispersant consisting of a polymer that contains a structural unit from a vinyl group-containing monocarboxylic acid (salt) and has a weight average molecular weight of 4,000 to 40,000 and a Mw/Mn of 1.2 to 2.0 is produced using a persulfate as an initiator, and using isopropyl alcohol as both a reaction solvent and a chain transfer agent. Patent Literatures 3 and 4 also disclose a same method as that in Patent Literature 2 wherein a dispersant is produced using a persulfate as an initiator, and using isopropyl alcohol as a reaction solvent and a chain transfer agent.

[PRIOR ART LITERATURE]

[PATENT LITERATURE]

[0003]

Patent Literature 1: JP A S60-174793

Patent Literature 2: JP A 2004-306022

Patent Literature 3: JP A 2004-315359

Patent Literature 4: WO 2004-087574

[SUMMARY OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0004]

However, the resulting dispersants by methods disclosed in Patent Literatures 2 to 4 do not exhibit satisfactory performance.

The invention was conceived in view of the above problem. An object of the present invention is to provide a dispersant for calcium carbonate, which leads to a calcium carbonate slurry having a reduced initial viscosity and being excellent in long-term dispersion stability and prevents a significant increase in viscosity of the slurry with passage of time, and a continuous production method thereof.

[0005]

The inventors conducted extensive studies in order to solve the above-mentioned problems and to obtain a dispersant for calcium carbonate in which an initial viscosity of a calcium carbonate slurry obtained by wet grinding or the like is low and there is no significant increase in viscosity with passage of time. The inventors found that a dispersant for calcium carbonate can be produced which leads to a calcium carbonate slurry having a reduced initial viscosity and being excellent in long-term dispersion stability and prevents a significant increase in viscosity of the slurry with passage of time by a method including a polymerization process in which a monomer containing acrylic acid, an isopropyl alcohol aqueous solution, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and the monomer is continuously polymerized at a reaction temperature between 68°C and 82°C, under condition that supply amounts of isopropyl alcohol, hypophosphite, persulfate, and sodium hydroxide based on 100 parts by mass of the monomer are respectively 15 to 100 parts by mass, 2.0 to 5.0 parts by mass, 0.5 to 2.0 parts by mass, and 5.0 to 20 parts by mass, and a neutralization process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from the monomer constituting a polymer obtained in the polymerization process is neutralized.

[0006]

The present invention is as follows.

1. A dispersant for calcium carbonate obtained by a method comprising sequentially a polymerization process and a neutralization process, characterized in that the polymerization process is a process in which a monomer containing acrylic acid, an isopropyl alcohol aqueous solution, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and the monomer is continuously polymerized, that a supply amount of isopropyl alcohol in the isopropyl alcohol aqueous solution is in the range from 15 to 100 parts by mass based on 100 parts by mass of the monomer, that a supply amount of the hypophosphite is in the range from 2.0 to 5.0 parts by mass based on 100 parts by mass of the monomer, that a supply amount of the persulfate is in the range from 0.5 to 2.0 parts by mass based on 100 parts by mass of the monomer, that a supply amount of the sodium hydroxide is in the range from 5.0 to 20 parts by mass based on 100 parts by mass of the monomer, that a reaction temperature in the polymerization process is between 68°C and 82°C, and that the neutralization process is a process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from the monomer constituting a polymer obtained in the polymerization process is neutralized.

2. The dispersant for calcium carbonate according to 1 above, wherein the method further comprises, between the polymerization process and the neutralization process, a concentration process in which the isopropyl alcohol is distilled off.

3. The dispersant for calcium carbonate according to 2 above, wherein the isopropyl alcohol recovered after the concentration process is used in the polymerization process.

4. The dispersant for calcium carbonate according to any one of 1 to 3 above, wherein a concentration of the isopropyl alcohol in the isopropyl alcohol aqueous solution is in the range from 15% to 55% by mass.

5. The dispersant for calcium carbonate according to any one of 1 to 4 above, wherein a content of the acrylic acid in the monomer is in the range from 80% to 100% by mass based on 100% by mass of a total amount of the monomer.

6. A continuous production method of the dispersant for calcium carbonate according to 1 above, characterized in that the method sequentially comprises a polymerization process and a neutralization process, wherein the polymerization process is a process in which a monomer containing acrylic acid, an isopropyl alcohol aqueous solution, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and the monomer is continuously polymerized, wherein a supply amount of isopropyl alcohol in the isopropyl alcohol aqueous solution is in the range from 15 to 100 parts by mass based on 100 parts by mass of the monomer, wherein a supply amount of the hypophosphite is in the range from 2.0 to

5.0 parts by mass based on 100 parts by mass of the monomer, wherein a supply amount of the persulfate is in the range from 0.5 to 2.0 parts by mass based on 100 parts by mass of the monomer, wherein a supply amount of the sodium hydroxide is in the range from 5.0 to 20 parts by mass based on 100 parts by mass of the monomer, wherein a reaction temperature in the polymerization process is between 68°C and 82°C, and wherein the neutralization process is a process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from the monomer constituting a polymer obtained in the polymerization process is neutralized.

7. The continuous production method of the dispersant for calcium carbonate according to 6 above, wherein the polymerization process is performed so that two or more continuous vessel-type reactors are installed in series.

8. The continuous production method of the dispersant for calcium carbonate according to 6 or 7 above, wherein the method further comprises, between the polymerization process and the neutralization process, a concentration process in which the isopropyl alcohol is distilled off.

9. The continuous production method of the dispersant for calcium carbonate according to 8 above, wherein a thin film evaporator is used in the concentration process.

10. The continuous production method of the dispersant for calcium carbonate according to 8 or 9 above, wherein the isopropyl alcohol recovered after the concentration process is used in the polymerization process.

11. The continuous production method of the dispersant for calcium carbonate according to any one of 6 to 10 above, wherein a concentration of the isopropyl alcohol in the isopropyl alcohol aqueous solution is in the range from 15% to 55% by mass.

12. The continuous production method of the dispersant for calcium carbonate according to any one of 6 to 11 above, wherein a content of the acrylic acid in the monomer is in the range from 80% to 100% by mass based on 100% by mass of a total amount of the monomer.

[EFFECT OF THE INVENTION]

[0007]

The dispersant for calcium carbonate of the present invention is excellent in dispersibility of calcium carbonate and exhibits excellent dispersibility and long-term dispersion stability particularly as a dispersant for wet grinding of calcium carbonate. In the dispersant for calcium carbonate of the present invention, since isopropyl alcohol that functions as a chain transfer agent is used as a solvent, a hypophosphite as a chain transfer agent and a persulfate as an initiator are used in combination, and sodium hydroxide is added, the amount of by-products

(e.g., phosphites and phosphates) produced from the hypophosphite and the amount of by-products (e.g., sulfates) produced from the persulfate are reduced. Use of the dispersant for calcium carbonate of the present invention leads to a calcium carbonate slurry that has low initial viscosity and does not show a significant increase in viscosity with passage of time.

In the case where the content of acrylic acid in the monomer is in the range from 80% to 100% by mass based on 100% by mass of a total amount of the monomer, the dispersant for calcium carbonate can more advantageously disperse calcium carbonate.

[0008]

The continuous production method of a dispersant for calcium carbonate of the present invention can efficiently produce a dispersant for calcium carbonate leading to a calcium carbonate slurry that exhibits low initial viscosity, and does not show a significant increase in viscosity with passage of time.

In the case where a concentration process in which isopropyl alcohol is evaporated is provided after polymerization process, a dispersant for calcium carbonate can be efficiently produced in which the amount of isopropyl alcohol is reduced.

In the case where the isopropyl alcohol recovered after the concentration process is used in the polymerization process, evaporated isopropyl alcohol can be reused in the polymerization process and need not be disposed of. Therefore, it is possible to provide a continuous method for producing a dispersant for calcium carbonate that can reduce cost, and achieve excellent production efficiency and environmental protection.

In the case where the content of the acrylic acid used in the polymerization process is in the range from 80% to 100% by mass based on 100% by mass of a total amount of the monomer, it is possible to efficiently produce a dispersant for calcium carbonate that can more advantageously disperse calcium carbonate.

[DESCRIPTION OF EMBODIMENTS]

[0009]

In the following, the dispersant for calcium carbonate of the present invention (hereinafter, referred to also as “dispersant” simply) and a continuous production method of a dispersant for calcium carbonate of the present invention are described in detail.

The present invention is a dispersant for calcium carbonate obtained by a production method (continuous production method) provided with a polymerization process and a neutralization process sequentially, and is characterized in that the polymerization process is a process in which a monomer containing acrylic acid, an aqueous solution of isopropyl alcohol, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and

the monomer is continuously polymerized, that supply amounts of the isopropyl alcohol contained in the isopropyl alcohol aqueous solution, the hypophosphite, the persulfate, and the sodium hydroxide are respectively 15 to 100 parts by mass, 2.0 to 5.0 parts by mass, 0.5 to 2.0 parts by mass, and 5.0 to 20 parts by mass, based on 100 parts by mass of the monomer, that a reaction temperature in the polymerization process is between 68°C and 82°C, and that the neutralization process is a process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from the monomer constituting a polymer obtained in the polymerization process (hereinafter referred to also as “a first polymer”) is neutralized.

The supply amount may be a supply amount per a unit time in the continuous production process.

In the description of the present invention, “(meth)acryl” means acryl and/or methacryl.

[0010]

The dispersant of the present invention is obtained by a method including the polymerization process and the neutralization process. The raw materials used for the production of the dispersant of the present invention are described below.

[0011]

In the polymerization process, the monomer that is subjected to polymerization includes at least acrylic acid. Specifically, the monomer may include only acrylic acid, or may further include a monomer other than acrylic acid.

The monomer other than acrylic acid (hereinafter referred to as “other monomer”) is not particularly limited so long as the monomer is copolymerizable with the acrylic acid. Examples of the other monomer include a radically-polymerizable vinyl-based monomer (polymerizable unsaturated compound). Examples of the vinyl-based monomer include an ethylenically unsaturated carboxylic acid other than acrylic acid, a neutralized salt of ethylenically unsaturated carboxylic acid, an alkyl (meth)acrylate compound, an aromatic vinyl compound, an acid anhydride, an amino group-containing vinyl compound, an amide group-containing vinyl compound, a sulfonic acid group-containing vinyl compound, a polyoxyalkylene group-containing vinyl compound, an alkoxy group-containing vinyl compound, a cyano group-containing vinyl compound, a cyanidated vinyl compound, a vinyl ether compound, a vinyl ester compound, a conjugated diene, and the like. These compounds may be used singly or in combination of two or more types thereof.

Among these, an alkyl (meth)acrylate compound and a polyoxyalkylene group-containing vinyl compound are preferable from the viewpoint of the properties (e.g., dispersibility and suppression of coloration) of the resulting dispersant.

[0012]

Examples of the ethylenically unsaturated carboxylic acid other than acrylic acid include methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, a half-ester of phthalic anhydride with an alkyl alcohol, a half-ester of itaconic anhydride with an alkyl alcohol, and the like.

[0013]

Examples of the neutralized salt of ethylenically unsaturated carboxylic acid include ethylenically unsaturated carboxylates obtained by neutralizing a carboxyl group in acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, and the like. The ethylenically unsaturated carboxylate may be an alkali metal salt, an alkaline-earth metal salt, an ammonium salt, an organic amine salt, or the like.

[0014]

Examples of the alkyl (meth)acrylate compound 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, benzyl (meth)acrylate, and the like.

[0015]

Examples of the aromatic vinyl compound include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α -methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-tert-butylstyrene, tert-butoxystyrene, vinyltoluene, vinylnaphthalene, halogenated styrene, styrenesulfonic acid, α -methylstyrenesulfonic acid, and the like.

[0016]

Examples of the acid anhydride include maleic anhydride, itaconic anhydride, citraconic anhydride, and the like.

[0017]

Examples of the amino group-containing vinyl compound 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, 3-(di-n-propylamino)propyl (meth)acrylate, and the like.

[0018]

Examples of the amide group-containing vinyl compound include (meth)acrylamide, N,N-dimethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, N-methylol(meth)acrylamide, and the like.

[0019]

Examples of the sulfonic acid group-containing vinyl compound include methallylsulfonic acid, acrylamide-2-methyl-2-propanesulfonic acid, and the like.

[0020]

Examples of the polyoxyalkylene group-containing vinyl compound include esters of (meth)acrylic acid and an alcohol having a polyoxyethylene group and/or a polyoxypropylene group, and the like.

[0021]

Examples of the alkoxy group-containing vinyl compound 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, 2-(n-butoxy)propyl (meth)acrylate, and the like.

[0022]

Examples of the cyano group-containing (meth)acrylate compound 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-cyano butyl (meth)acrylate, 6-cyano hexyl (meth)acrylate, 2-ethyl-6-cyano hexyl (meth)acrylate, 8-cyano octyl (meth)acrylate, and the like.

[0023]

Examples of the cyanidated vinyl compound include acrylonitrile, methacrylonitrile, ethacrylonitrile, and the like.

[0024]

Examples of the vinyl ether compound include vinyl methyl ether, vinyl ethyl ether, vinyl n-butyl ether, vinyl phenyl ether, vinyl cyclohexyl ether, and the like. These compounds may be used singly or in combination of two or more types thereof.

Examples of the vinyl ester compound include vinyl formate, vinyl acetate, vinyl propionate, and the like.

[0025]

Examples of the conjugated diene 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, chloroprene, and the like.

[0026]

Other examples include a maleimide compound such as maleimide, N-methylmaleimide, N-butylmaleimide, N-phenylmaleimide, and N-cyclohexylmaleimide; a maleate compound; an itaconate compounds; a N-vinyl heterocyclic compound such as vinylpyridine; and the like.

[0027]

Among these, methyl acrylate and butyl acrylate are preferable. A dispersant that advantageously suppresses coloration can be obtained when using methyl acrylate, butyl acrylate, or the like in combination with acrylic acid.

[0028]

In the case where the monomer used in the polymerization process includes other monomer other than acrylic acid, the content of acrylic acid in the monomer is preferably 80% or more by mass, more preferably 90% or more by mass, and further preferably 95% or more by mass. It is particularly preferable that the monomer is acrylic acid (100% by mass) in the present invention. When the content of acrylic acid in the monomer is 80% or more by mass, the resulting dispersant exhibits sufficient solubility in water.

[0029]

In the polymerization process, the hypophosphite is used as a chain transfer agent. The hypophosphite is not particularly limited so long as the hypophosphite is a compound having a chain transfer effect. Specific examples of the hypophosphite include sodium hypophosphite, potassium hypophosphite, lithium hypophosphite, calcium hypophosphite, magnesium hypophosphite, barium hypophosphite, and the like. These compounds may be used singly or in combination of two or more types thereof. Among these, sodium hypophosphite is preferable.

[0030]

A supply amount (usage amount) of the hypophosphite in the polymerization process is in the range from 2.0 to 5.0 parts by mass, preferably from 2.5 to 4.5 parts by mass, and more preferably from 3.0 to 4.5 parts by mass based on 100 parts by mass of the monomer. When the supply amount of the hypophosphite is within the above range, continuous polymerization of the monomer can be efficiently performed. When the usage amount of the hypophosphite is not more than 5.0 parts by mass, a dispersant having a small content of by-produced phosphite and phosphate is obtained, whereby there can be provided a dispersant in which an initial viscosity of a calcium carbonate slurry obtained by wet grinding is low, a significant viscosity increase with passage of time is suppressed, and long-term dispersion stability is excellent. On

the other hand, if the supply amount of the hypophosphite is large (for example, more than 5.0 parts by mass of the hypophosphite is used), the initial viscosity of a calcium carbonate slurry is high, and the viscosity is significantly increased with passage of time. It is inferable that this is because phosphite and phosphate as by-products produced from the hypophosphite increase, and the by-products and calcium carbonate form a hardly soluble compound to thereby lead to viscosity increase.

[0031]

In the polymerization process, the persulfate is used as an initiator (radical initiator). Examples of the persulfate include sodium persulfate, ammonium persulfate, potassium persulfate, and the like. These compounds may be used singly or in combination of two or more types thereof. It is preferable to use sodium persulfate or potassium persulfate since a volatile component is rarely generated in the neutralization process performed after the polymerization process.

[0032]

A supply amount (usage amount) of the persulfate in the polymerization process is in the range from 0.5 to 2.0 parts by mass, preferably from 0.6 to 1.8 parts by mass, and more preferably from 0.8 to 1.5 parts by mass based on 100 parts by mass of the monomer. When the supply amount of the persulfate is within in the above range, an unreacted monomer can be reduced. When the supply amount of the persulfate is not more than 2.0 parts by mass, a dispersant having a small content of by-produced sulfate can be provided. On the other hand, when the supply amount of the sulfate is large (for example, more than 2.0 parts by mass of the persulfate is used), an initial viscosity of a calcium carbonate slurry is high, and the viscosity is significantly increased with passage of time. It is inferable that this is because sulfate as by-products produced from the persulfate increases in the same case as that of the hypophosphite and the by-products and calcium carbonate form a hardly soluble compound to thereby lead to viscosity increase.

[0033]

In the polymerization process, sodium hydroxide is used as a basic compound. The sodium hydroxide is added in order to prevent oxidation of the hypophosphite in the polymerization process. The hypophosphite is oxidized to generate a phosphite and a phosphate as by-products. In the present invention, use of sodium hydroxide in the polymerization process efficiently suppresses oxidization of hypophosphite used as a chain transfer agent.

[0034]

A supply amount (usage amount) of sodium hydroxide in the polymerization process

is in the range from 5.0 to 20 parts by mass, and preferably from 7.0 to 15 parts by mass based on 100 parts by mass of the monomer. When the supply amount of sodium hydroxide is within the above range, oxidization of hypophosphite in the polymerization process can be efficiently suppressed, and a dispersant can be produced in which an initial viscosity of a calcium carbonate slurry obtained by wet grinding is low, a significant viscosity increase with passage of time is suppressed, and long-term dispersion stability is excellent.

[0035]

In the polymerization process, an isopropyl alcohol aqueous solution is used as a solvent.

Isopropyl alcohol also functions as a chain transfer agent in the polymerization process. Therefore, the isopropyl alcohol aqueous solution is used as a reaction solvent and a chain transfer agent.

A concentration of isopropyl alcohol in the isopropyl alcohol aqueous solution is preferably 5% or more by mass and 90% or less by mass, more preferably in the range from 10% to 80% by mass, further preferably from 15% to 60% by mass, and particularly from 15% to 55% by mass. The concentration thereof may be from 17% to 50% by mass, or from 20% to 40% by mass.

When the isopropyl alcohol concentration is 5% or more by mass, the isopropyl alcohol effectively exhibits the chain transfer effect (i.e., effectively functions as the chain transfer agent).

[0036]

In the polymerization process, a supply amount (usage amount) of isopropyl alcohol contained in the isopropyl alcohol aqueous solution is in the range from 15 to 100 parts by mass, preferably from 16 to 90 parts by mass, and more preferably from 17 to 80 parts by mass based on 100 parts by mass of the monomer. When isopropyl alcohol is used in an amount of 15 parts or more by mass, the chain transfer effect of isopropyl alcohol is effectively exhibited. When isopropyl alcohol is used in an amount of 100 parts or less by mass, a solubility of the raw material may be improved.

[0037]

According to the polymerization process, a monomer containing acrylic acid is polymerized in the presence of the hypophosphite, persulfate, and sodium hydroxide, while using an isopropyl alcohol aqueous solution as a reaction solvent to form a first polymer having a structural unit derived from the monomer. A weight-average molecular weight of the first polymer is preferably in the range from 3,000 to 20,000, more preferably from 4,000 to 10,000, and further preferably from 4,500 to 8,500. The weight-average molecular weight can be

measured by gel permeation chromatography (GPC), using a standard material such as sodium polyacrylate.

The first polymer having the weight-average molecular weight within the above range leads to a dispersant excellent in dispersibility of dispersing calcium carbonate, and there can be provided a dispersant in which an initial viscosity of a calcium carbonate slurry becomes low, and a significant viscosity increase with passage of time can be suppressed.

[0038]

Use of isopropyl alcohol having a function of a chain transfer agent as a solvent, a hypophosphite as a chain transfer agent, a persulfate as a polymerization initiator, and sodium hydroxide suppressing oxidization of the hypophosphite in the polymerization process leads to continuous polymerization and a dispersant can be efficiently obtained. When the dispersant is used, a calcium carbonate slurry can be obtained in which an initial viscosity is low and a significant viscosity increase with passage of time can be suppressed. In this regard, when usage amounts of the hypophosphite and persulfate are reduced and sodium hydroxide is used, an amount of by-products such as a phosphite and phosphate generated from hypophosphite and a sulfate generated from persulfate is small, formation of a hardly soluble compound from the by-products and calcium carbonate can be suppressed, whereby an initial viscosity of a slurry becomes low, and a significant viscosity increase with passage of time can be suppressed.

[0039]

The reaction temperature employed in the polymerization process is between 68°C and 82°C, and more preferably between 70°C and 80°C. When the reaction temperature is 82°C or lower, polymerization proceeds smoothly, and oxidation of hypophosphorous acid (chain transfer agent) to phosphites and phosphates can be suppressed, so that a dispersant containing only a small amount of by-product phosphites and phosphates can be obtained. When the reaction temperature is 68°C or higher, a dispersant containing only a small amount of unreacted monomers can be obtained.

[0040]

According to the polymerization process in the present invention, a reactor is used. The polymerization process is preferably conducted using a plurality of reactors because monomers are continuously polymerized, and it is preferable that reactors are connected in series for the polymerization. In the case of using the connected reactors (continuous reactor), the number of the reactors is preferably not less than two and normally not more than ten. When the continuous reactor is used in which two or more reactors are connected in series, the residence time of the monomer in the polymerization process is uniformized, and the amount of unreacted monomers can be reduced. Namely, if a single reactor is used, a monomer going

through the polymerization process (unreacted monomer) before the polymerization of the monomer in the polymerization process is not satisfactorily completed may be generated. If more than ten continuous reactors are installed, it is economically inefficient.

[0041]

The reactor may be a vessel-type reactor. When the vessel-type reactor is used in the polymerization process according to the present invention, the monomer can be efficiently polymerized. In the present invention, it is preferable to connect a plurality of vessel-type reactors in series. When a reactor in which a plurality of vessel-type reactors are connected in series (hereinafter, referred to as "continuous vessel-type reactor" simply) is used in the polymerization process according to the present invention, continuous polymerization of the monomer can be efficiently performed.

A publicly known reactor can be used as the vessel-type reactor, and preferred is a reactor having a mixer and a device for temperature control. The stirrer is not specifically limited so long as a publicly known stirring blade is installed, and examples of the stirring blade include an anchor blade, a paddle blade, a propeller blade, a turbine blade, a ribbon blade, a large flat-plate blade, and the like. Examples of the device for temperature control include a jacket, an inner coil, a well-known internal and/or external heat exchanger such as a plate type heat exchanger. For the purpose of enhancing stirring efficiency and so on, a baffle and the like may be arranged in the reactor if necessary.

[0042]

When the polymerization process employs, for example, n reactors, assuming that an initial reactor in the polymerization process is a first reactor (upstream side), the next reactor is a second reactor, and the last reactor in the polymerization process is an n -th reactor (downstream side), into the first reactor, at least the monomer, isopropyl alcohol aqueous solution, hypophosphite, persulfate, and sodium hydroxide as raw materials are continuously charged.

When the raw material is supplied to the reactor, all the raw materials to be supplied may be charged to the first reactor, or a part of the raw material may be charged to the first reactor and the remaining raw material except for the raw material supplied to the first reactor may be charged to other reactors. Among these, it is preferable to supply all the raw materials to the first reactor.

Into the second to n -th reactors, each of reaction liquid from the first to the $(n-1)$ -th reactors connected respectively upstream side and a remaining raw material in the case where a part of the raw material is supplied to the first reactor are charged. Before start of the polymerization process, an isopropyl alcohol aqueous solution may be previously introduced to

the second to n-th reactors.

A reaction liquid obtained in the n-th reactor is a reaction liquid containing a first polymer obtained in the polymerization process.

In the first to n-th reactors, temperatures (polymerization temperature) in reactors may be the same or may be different from each other so long as they are between 68°C and 82°C.
[0043]

In the case where the continuous vessel-type reactor including n reactors is used in the polymerization process, the total mean residence time of a reaction liquid in the continuous vessel-type reactor is preferably in the range from 100 to 450 minutes, and more preferably from 140 to 330 minutes. The mean residence time in each reactor is not specifically limited, and the mean residence time is suitably selected so that the total mean residence time in the continuous vessel-type reactor is within the above range.

For example, when a continuous vessel-type reactor including two reactors is used, the mean residence time in the first reactor is preferably in the range from 60 to 240 minutes, and more preferably from 80 to 180 minutes. The mean residence time in the second reactor is preferably from 40 to 210 minutes, and more preferably from 60 to 150 minutes. When the mean residence times in the first and second reactors are within the above range in this case, the amount of unreacted monomers can be reduced, and, oxidization of the hypophosphite can be suppressed.

[0044]

The neutralization process is a process in which a carboxyl group included in a structural unit derived from the monomer constituting the first polymer obtained in the polymerization process is neutralized. According to the neutralization process, a dispersant can be obtained which contains an acryl-based polymer in which a part of carboxyl groups is neutralized. In the neutralization process, a dispersant having pH from 3 to 8 can be obtained.

[0045]

In the neutralization process, the carboxyl groups are neutralized using a basic compound. The basic compound is not particularly limited so long as the basic compound can neutralize a carboxyl group. Examples of the basic compound include an inorganic basic compound and an organic basic compound. These compounds may be used singly or in combination of two or more types thereof.

Examples of the inorganic basic compound include an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide, and lithium hydroxide; an alkaline-earth metal hydroxide such as calcium hydroxide and magnesium hydroxide; aqueous ammonia, and the like.

Examples of the organic basic compound include an organic amine compound such as monoethanolamine and triethanolamine. Among these, an alkali metal hydroxide is preferable since a volatile component is generated to only a small extent. Sodium hydroxide is more preferable.

[0046]

In the neutralization process, the neutralization rate of the carboxyl groups included in the first polymer is in the range from 15% to 95% by mol, and preferably from 20% to 90% by mol. When the neutralization rate is in the range from 15% to 95% by mol, a dispersant can be obtained which advantageously disperses calcium carbonate.

[0047]

In the present invention, a reactor can be used in the neutralization process. The same vessel-type reactor as in the reactor used in the polymerization process can be used as the reactor.

In the case where a vessel-type reactor is used in the neutralization process and a continuous vessel-type reactor including two or more reactors is used in the polymerization process, when a vessel-type reactor for the neutralization process is connected to a continuous vessel-type reactor for the polymerization process (including n reactors), in other words, a continuous vessel-type reactor including three or more reactors connected in series is used, the polymerization process and neutralization process can be performed continuously and efficiently. When the polymerization process and neutralization process are performed using the continuous vessel-type reactor in which three or more vessel-type reactors are connected in series, a dispersant can be obtained efficiently.

[0048]

The acryl-based polymer contained in the dispersant is a polymer in which a monomer containing acrylic acid is polymerized and a part of carboxyl groups derived from the monomer is neutralized. A part of the terminal or the like of the polymer may include a constitution derived from the hypophosphite or persulfate used in the polymerization.

A weight average molecular weight of the acryl-based polymer is preferably in the range from 4,500 to 8,500, and more preferably from 5,000 to 8,000. The weight-average molecular weight can be, as mentioned above, measured by GPC using a standard material such as sodium polyacrylate. When the weight average molecular weight of the acryl-based polymer is within the above range, a dispersant can be obtained which advantageously disperses calcium carbonate. And when the dispersant is used, a calcium carbonate slurry can be obtained in which an initial viscosity is low and a significant viscosity increase with passage of time can be suppressed.

[0049]

For the dispersant of the present invention, in addition to the polymerization process and neutralization process, a concentration process may be provided after the polymerization process. The concentration process is preferably provided between the polymerization process and neutralization process.

[0050]

The concentration process is a process in which isopropyl alcohol is distilled off from a reaction liquid containing the first polymer obtained in the polymerization process to prepare a concentrated composition containing reduced isopropyl alcohol.

[0051]

In the concentration process, the reaction system is subjected to depressurizing and/or heating to distill isopropyl alcohol out of the reaction system. Isopropyl alcohol can thus be evaporated off from the reaction liquid. Isopropyl alcohol is normally evaporated off as an azeotrope with water. Therefore, isopropyl alcohol is distilled off from the reaction liquid as an aqueous solution thereof to form a concentrated composition having a reduced isopropyl alcohol content and a reduced water content.

[0052]

In the concentration process, isopropyl alcohol may be distilled off by an arbitrary method. For example, when the reaction system is subjected to depressurizing, and the internal temperature of the reaction system is kept at a temperature equal to or higher than the azeotropic temperature of isopropyl alcohol to evaporate water and isopropyl alcohol off from the reaction system.

[0053]

In the concentration process, an isopropyl alcohol aqueous solution can be subjected to distillation with a thin film evaporator. The thin film evaporator is a device for converting a reaction liquid obtained in the polymerization process into a thin film and evaporating and distilling the reaction liquid under vacuum at lower temperature while suppressing thermal effect.

When the thin film evaporator is used in the concentration process, water may be suitably added to the thin film evaporator to distill isopropyl alcohol off as an azeotrope with water. According to the use of the thin film evaporator, denaturation of the reaction liquid in the concentration process can be suppressed, and isopropyl alcohol can be distilled off efficiently.

[0054]

A content of isopropyl alcohol in the concentrated composition obtained by the

concentration process is preferably 1% or less by mass, more preferably 5,000 ppm or less by mass, further preferably 2,000 ppm or less by mass, and particularly 1,000 ppm or less by mass. [0055]

The isopropyl alcohol aqueous solution evaporated in the concentration process may be recovered. The recovered isopropyl alcohol aqueous solution may be repeatedly used in the polymerization process. When the isopropyl alcohol aqueous solution is reused, evaporated isopropyl alcohol need not be disposed of. Therefore, it is possible to provide a dispersant for calcium carbonate that can reduce cost, and achieve excellent production efficiency and environmental protection, and a method for producing a dispersant for calcium carbonate.

In the case of recovering an isopropyl alcohol aqueous solution, the concentration of isopropyl alcohol after recovery may differ from the one before recovery. Specifically, since isopropyl alcohol is evaporated off as an azeotrope of isopropyl alcohol and water, and then recovered, the concentration of isopropyl alcohol in the isopropyl alcohol aqueous solution recovered becomes normally about 60% or lower by mass, even if a high-concentration isopropyl alcohol aqueous solution is used in the polymerization process.

In the polymerization process, it is preferable to use the isopropyl alcohol aqueous solution having a constant isopropyl alcohol concentration in order to improve the production efficiency, even when the isopropyl alcohol aqueous solution is reused. Specifically, when the polymerization process is performed in a state in which the concentration of isopropyl alcohol in the isopropyl alcohol aqueous solution is 60% or higher by mass, the isopropyl alcohol concentration in the recovered isopropyl alcohol aqueous solution may be reduced due to evaporation. In this case, it is necessary to concentrate the recovered isopropyl alcohol aqueous solution so that the isopropyl alcohol aqueous solution has the original isopropyl alcohol concentration. On the other hand, the isopropyl alcohol concentration in the recovered isopropyl alcohol aqueous solution may be higher than the one before recovery. In the case where the isopropyl alcohol concentration in the recovered isopropyl alcohol aqueous solution is higher than the one before recovery, the isopropyl alcohol concentration may be adjusted by adding water. However, when the recovered isopropyl alcohol aqueous solution is subjected to concentration so that the isopropyl alcohol aqueous solution has the original isopropyl alcohol concentration, it is necessary to provide concentration equipment, so that the production efficiency decreases.

Regarding the concentration of isopropyl alcohol in the isopropyl alcohol aqueous solution, when the concentration of isopropyl alcohol is lower than that in the isopropyl alcohol aqueous solution by the concentration process, the resulting isopropyl alcohol aqueous solution can be reused. The isopropyl alcohol concentration when recovering or reusing the isopropyl

alcohol aqueous solution is preferably in the range from 15% to 55% by mass, more preferably from 17% to 50% by mass, and particularly from 20% to 40% by mass. It is noted that the recovered isopropyl alcohol aqueous solution is preferably reused in the polymerization process after adjusting the isopropyl alcohol concentration.

[0056]

When the concentrated composition obtained in the concentration process is subjected to the neutralization process, a part of carboxyl groups in the first polymer is neutralized to form a dispersant containing an acryl-based polymer.

[0057]

In the present invention, examples of a continuous production process (production system) consisting of the polymerization process, concentration process, and neutralization process include a method in which a plurality of vessel-type reactors and a thin film evaporator are connected in series.

In a preferred embodiment of the present invention, a continuous vessel-type reactor in which two or more vessel-type reactors are connected is used in the polymerization process, and a thin film evaporator is used in the concentration process. Additionally, in the neutralization process, a vessel-type reactor can be used. In the present invention, it is preferable to provide a continuous production process (production system) in which a continuous vessel-type reactor for the polymerization process, a thin film evaporator for the concentration process, and a vessel-type reactor for the neutralization process are provided connecting in series in this order. Such a continuous production process leads to a continuously and efficiently production of a dispersant.

[0058]

The dispersant of the present invention is one obtained by a method having the polymerization process, neutralization process and the like. The dispersant may be a solution in which the acryl-based polymer is dissolved in an aqueous medium, or may be a dispersion in which the acryl-based polymer is dispersed in an aqueous medium. The aqueous medium may contain water, and be only water or a mixture containing water.

[0059]

The dispersant of the present invention may be (a) a reaction liquid obtained by the polymerization process and neutralization process, or (b) a reaction liquid obtained by the polymerization process, concentration process and neutralization process. Among these, the reaction liquid (b) is preferable for the dispersant since the dispersant can be efficiently obtained. These dispersants may further include an aqueous medium.

[0060]

The reaction liquid (b) is normally an aqueous solution in which the acryl-based polymer is dissolved in an aqueous medium, and may include the phosphite used in the polymerization process and/or by-products produced from the phosphite, the persulfate used in the polymerization process and/or by-products produced from the persulfate, and the basic compound used in the neutralization process. The reaction liquid (b) may also include isopropyl alcohol in an amount corresponding to the amount after the concentration process.

A content of isopropyl alcohol in the reaction liquid (b) may be 1% or less by mass, preferably 5,000 ppm or less by mass, more preferably 2,000 ppm or less by mass, and further preferably 1,000 ppm or less by mass.

[0061]

When the dispersant of the present invention is the reaction mixture (b), pH and solid content of the dispersant are not particularly limited. The pH of the dispersant is preferably in the range from 3 to 8, and more preferably from 3 to 7. The solid content in the dispersant is preferably in the range from 35 to 55%, and more preferably 40 to 50%.

[0062]

The dispersant of the present invention may further include an additional component such as antifoaming agent and preservative.

Examples of the antifoaming agent include a polyether compound, a mineral oil compound, a silicone compound, an amide compound, and the like. When the dispersant of the present invention includes the antifoaming agent, the content thereof is preferably in the range from 0.01 to 1.0 part by mass based on 100 parts by mass of the acryl-based polymer.

[0063]

Examples of the preservative include an isothiazoline compound, a paraben, and the like. When the dispersant of the present invention includes the preservative, the content thereof is preferably in the range from 0.001 to 1.0 part by mass based on 100 parts by mass of the acryl-based polymer.

[0064]

The dispersant of the present invention may be a solution or a dispersion in which the acryl-based polymer, and an optional additional component are included in an aqueous medium.

In the case where the dispersant of the present invention contains the additional component, the additional component is added and mixed with the aqueous medium and the acryl-based polymer. The mixing method is not particularly limited and may be a publicly known method.

[0065]

In the case of preparing a calcium carbonate slurry using the dispersant of the present

invention, the dispersant is preferably used so that the content of the acryl-based polymer is in the range from 0.1 to 10.0 parts by mass, and the content of the aqueous medium is in the range from 25 to 100 parts by mass, based on 100 parts by mass of calcium carbonate.

After that, the dispersant mixture containing calcium carbonate and the acryl-based polymer is subjected to wet grinding by a known method to produce a calcium carbonate slurry. [0066]

The dispersant of the present invention is excellent in dispersibility of calcium carbonate, and is suitably used as a dispersant for wet grinding of calcium carbonate to obtain a calcium carbonate slurry. Use of the dispersant for calcium carbonate of the present invention leads to a calcium carbonate slurry that has low initial viscosity, that does not show a significant increase in viscosity with passage of time, and exhibits excellent long-term dispersion stability. [0067]

In the case where the dispersant of the present invention contains the additional component, the acryl-based polymer can be mixed with the additional component that is optionally added. When the dispersant of the present invention is an aqueous solution or a dispersion that is based on an aqueous medium containing the acryl-based polymer, the additional component may be mixed into the aqueous solution or the dispersion. The mixing method is not particularly limited and may be a publicly known method.

[EXAMPLES]

[0068]

Hereinafter, although Examples of the present invention will be described along with Comparative Examples, the scope of the invention is obviously not limited to these examples. Note that in the following examples, “part” and “%” are mass standard unless otherwise designated.

The term “Mw” used in Examples, and Comparative Examples refers to a weight average molecular weight. The Mw was measured by gel permeation chromatography (GPC). “HLC8020 system” (manufactured by Tosoh Corporation), and columns “G4000PW” (×1), “G3000PW” (×1), “G2500PW” (×1) (manufactured by Tosoh Corporation) were used for GPC. A 0.1M NaCl + phosphate buffer (pH7) was used as an eluent, and a calibration curve was drawn using sodium polyacrylate (manufactured by Sowa Scientific Corporation).

[0069]

In Examples, and Comparative Examples, a viscosity of the ground calcium carbonate slurry after wet grinding, and a viscosity of the slurry after being allowed to stand at 25°C for 7 days were measured at a temperature of 25°C and a rotational speed of 60 rpm using Brookfield

viscometer.

A median size of the ground calcium carbonate slurry after wet grinding, and an integrated value of calcium carbonate with a diameter smaller than 1.32 μm were measured using a laser diffraction/scattering particle size distribution analyzer “LA-910” manufactured by Horiba Ltd.

[0070]

<Preparation of dispersant for calcium carbonate and preparation of ground calcium carbonate slurry>

Example 1-1 (Preparation of dispersant 1-1 and preparation of slurry using dispersant 1-1)

Three flasks provided with a mixer and a condenser, and a thin film evaporator were prepared, and the three flasks were first to third flasks. The three flasks and the thin film evaporator were arranged in series in order of the first flask, the second flask, the thin film evaporator, and the third flask, and the flow from a raw material composition to a reaction product was performed in this order.

First, the first flask was charged with 1,360 g of an aqueous solution of an isopropyl alcohol (hereinafter, referred to also as “IPA”) at a concentration of 35% and was kept at a temperature of 80°C. The second flask was charged with 1,360 g of an aqueous solution of an IPA at a concentration of 35% and was kept at a temperature of 80°C. Further, the third flask was charged with 1,360 g of deionized water and was kept at 80°C.

After that, acrylic acid (hereinafter, also referred to as “AA”) was supplied into the first flask at a rate of 4.5 g per minute, an aqueous solution of an IPA at a concentration of 35% was supplied into the first flask at a rate of 9.0 g per minute, an aqueous solution of a sodium hypophosphite at a concentration of 30% was supplied into the first flask at a rate of 0.55 g per minute, an aqueous solution of a sodium hydroxide at a concentration of 48% was supplied into the first flask at a rate of 0.70 g per minute, and an aqueous solution of a sodium persulfate at a concentration of 15% was supplied into the first flask at a rate of 0.30 g per minute. A reaction liquid in the first flask was transferred to the second flask at a rate of 15.1 g per minute.

Thus, the liquid volume in the first flask was kept to be 1,360 g, and the mean residence time of the reaction liquid in the first flask was determined as 90 minutes. Further, the reaction liquid in the second flask was transferred to the thin film evaporator at 15.1 g per minute while keeping the liquid volume at 1,360 g, and the mean residence time of the reaction liquid in the second flask was determined as 90 minutes. Meanwhile, at the thin film evaporator, IPA was vacuum-distilled off at a rate of 7.9 g per minute while supplying

deionized water to the thin film evaporator at a rate of 4.9 g per minute, and a concentrated liquid (in which the IPA aqueous solution was reduced) discharged from the thin film evaporator was transferred to the third flask. Then, into the third flask, an aqueous solution of a sodium hydroxide at a concentration of 48% was supplied so that the neutralization rate of the reaction liquid was 22 mol%. The liquid in the third flask was discharged outside the system so that the liquid volume was kept at 1,360 g. Once the operation was continued for 20 hours, and the liquid discharged from the third flask was recovered to obtain a dispersant 1-1 having a solid content of 40% and pH of 4. Mw of an acryl-based polymer 1-1 contained in the dispersant 1-1 was 6,200. The amount of each raw material used in the preparation of the dispersant, the concentration of each raw material, a ratio of each raw material based on 100 parts of the monomer, and so on are shown in Table 1.

[0071]

17 g of the dispersant 1-1 obtained by the above operation, 320 g of ion-exchanged water, and 900 g of a ground calcium carbonate ("Tankaru A" produced by Maruo Calcium Co., Ltd.) were introduced into a cylindrical vessel and lightly mixed to be uniformly adapted. Subsequently, 3,000 g of a medium (ceramic beads of 1 mm ϕ) was introduced into the cylindrical vessel and mixed for 50 minutes at a rotational speed of 1,000 rpm to be subjected to wet grinding.

After that, the mixture was subjected to filtration using a filter cloth having 200 ME and recovering to obtain a slurry. An ion-exchanged water was added to the slurry to adjust the solid content to 75% to obtain a ground calcium carbonate slurry. Then, the viscosity of the slurry of the day of wet grinding and the viscosity of the slurry after being left standing for 7 days at a temperature of 25°C were measured using Brookfield viscometer under conditions of 25°C and 60 rpm. The slurry viscosity of the day of wet grinding was 210 mPa·s, and the slurry viscosity after 7 days was 2,000 mPa·s.

A median size of the slurry of the day of wet grinding and an integrated value of calcium carbonate with a diameter smaller than 1.32 μ m were measured using a laser diffraction/scattering particle size distribution analyzer "LA-910" manufactured by Horiba Ltd. The median size was 0.67 μ m, and the integrated value with a diameter smaller than 1.32 μ m was 100%. Those results are shown in Table 1.

In the following Examples and Comparative Examples, the amount of each raw material used in the preparation of the dispersant, the concentration of each raw material, a ratio of each raw material based on 100 parts of the monomer, and so on are shown in Tables 1 to 4. Further, in the following Examples and Comparative Examples, Mw of an acryl-based polymer contained in a dispersant, the viscosity of a ground calcium carbonate slurry after wet grinding,

the viscosity of a slurry after left standing for seven days at 25°C, the median size of the ground calcium carbonate slurry after wet grinding, and the integrated value of calcium carbonate with a diameter smaller than 1.32 μm in the slurry after wet grinding were measured in the same manner as those in Example 1-1, and the measured results were shown in Tables 1 to 4. The amount of IPA distilled by the thin film evaporator and supply amount of deionized water were adjusted according to each polymerization condition so that the solid content of the resulting dispersant was 40%.

[0072]

Example 1-2 (Preparation of dispersant 1-2 and preparation of slurry using dispersant 1-2)

In this Example 1-2, a dispersant 1-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 1-1 in Example 1-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 1-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 1-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Example 1-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, and the liquid discharged from the third flask was recovered to obtain a dispersant 1-1 which contains an acryl-based polymer 1-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 1-2 in the same manner as those in Example 1-1.

[0073]

Example 2-1 (Preparation of dispersant 2-1 and preparation of slurry using dispersant 2-1)

Example 2-1 was performed similarly to Example 1-1 except that an aqueous solution of IPA at a concentration of 22% was supplied to the first flask at 9.0 g per minute instead of using the aqueous solution of IPA at a concentration of 35% in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 2-1 which contains an acryl-based polymer 2-1 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 2-1 in the same manner as those in Example 1-1.

[0074]

Example 2-2 (Preparation of dispersant 2-2 and preparation of slurry using dispersant 2-2)

In this Example 2-2, a dispersant 2-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 2-1 in Example 2-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 2-1 was measured, the IPA concentration was 25%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 2-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 22%. The operation of Example 2-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 2-2 which contains an acryl-based polymer 2-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 2-2 in the same manner as those in Example 2-1.

[0075]

Example 3-1 (Preparation of dispersant 3-1 and preparation of slurry using dispersant 3-1)

Example 3-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hypophosphite at a concentration of 30% to the first flask was 0.65 g per minute instead of 0.55 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 3-1 which contains an acryl-based polymer 3-1 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 3-1 in the same manner as those in Example 1-1.

[0076]

Example 3-2 (Preparation of dispersant 3-2 and preparation of slurry using dispersant 3-2)

In this Example 3-2, a dispersant 3-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 3-1 in Example 3-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 3-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 3-1, and the IPA aqueous solution was obtained in the form of an

aqueous solution of IPA at a concentration of 35%. The operation of Example 3-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 3-2 which contains an acryl-based polymer 3-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 3-2 in the same manner as those in Example 3-1.

[0077]

Example 4-1 (Preparation of dispersant 4-1 and preparation of slurry using dispersant 4-1)

Example 4-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hydroxide at a concentration of 48% to the first flask was 1.08 g per minute instead of 0.7 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 4-1 which contains an acryl-based polymer 4-1 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 4-1 in the same manner as those in Example 1-1.

[0078]

Example 4-2 (Preparation of dispersant 4-2 and preparation of slurry using dispersant 4-2)

In this Example 4-2, a dispersant 4-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 4-1 in Example 4-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 4-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 4-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Example 4-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 4-2 which contains an acryl-based polymer 4-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 4-2 in the same manner as those in Example 4-1.

[0079]

Example 5-1 (Preparation of dispersant 5-1 and preparation of slurry using dispersant 5-1)

Example 5-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium persulfate at a concentration of 15% to the first flask was 0.45 g per minute instead of 0.30 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 5-1 which contains an acryl-based polymer 5-1 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 5-1 in the same manner as those in Example 1-1.

[0080]

Example 5-2 (Preparation of dispersant 5-2 and preparation of slurry using dispersant 5-2)

In this Example 5-2, a dispersant 5-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 5-1 in Example 5-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 5-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 5-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Example 5-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 5-2 which contains an acryl-based polymer 5-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 5-2 in the same manner as those in Example 5-1.

[0081]

Example 6-1 (Preparation of dispersant 6-1 and preparation of slurry using dispersant 6-1)

Example 6-1 was performed similarly to Example 1-1 except that temperatures (polymerization temperatures) held in the first, second, and third flasks in Example 1-1 were set to 75°C instead of 80°C. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 6-1 which contains an acryl-based polymer 6-1 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 6-1 in the same manner as those in Example 1-1.

[0082]

Example 6-2 (Preparation of dispersant 6-2 and preparation of slurry using dispersant

6-2)

In this Example 6-2, a dispersant 6-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 6-1 in Example 6-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 6-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 6-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Example 6-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 6-2 which contains an acryl-based polymer 6-2 and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 6-2 in the same manner as those in Example 6-1.

[0083]

Example 7-1 (Preparation of dispersant 7-1 and preparation of slurry using dispersant 7-1)

Example 7-1 was performed similarly to Example 1-1 except that the neutralization rate of the reaction liquid in the third flask by the aqueous solution of sodium hydroxide at a concentration of 48% in Example 1-1 was set to 40 mol% instead of 22 mol%. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 7-1 which contains an acryl-based polymer 7-1 and has a solid content of 40% and pH of 5.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 7-1 in the same manner as those in Example 1-1.

[0084]

Example 7-2 (Preparation of dispersant 7-2 and preparation of slurry using dispersant 7-2)

In this Example 7-2, a dispersant 7-2 was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 7-1 in Example 7-1.

When the IPA concentration of the aqueous solution of IPA recovered in Example 7-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Example 7-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Example 7-1 was

continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 7-2 which contains an acryl-based polymer 7-2 and has a solid content of 40% and pH of 5.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 7-2 in the same manner as those in Example 7-1.

[0085]

Comparative Example 1-1 (Preparation of dispersant 1-1C and preparation of slurry using dispersant 1-1C)

Comparative Example 1-1 was performed similarly to Example 1-1 except that an aqueous solution of IPA at a concentration of 6.7% was used instead of the aqueous solution of IPA at a concentration of 35% in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 1-1C which contains an acryl-based polymer 1-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 1-1C in the same manner as those in Example 1-1.

[0086]

Comparative Example 1-2 (Preparation of dispersant 1-2C and preparation of slurry using dispersant 1-2C)

In this Comparative Example 1-2, a dispersant 1-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 1-1C in Comparative Example 1-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 1-1 was measured, the IPA concentration was 10%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 1-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 6.7%. The operation of Comparative Example 1-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 1-2C which contains an acryl-based polymer 1-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 1-2C in the same manner as those in Comparative Example 1-1.

[0087]

Comparative Example 2-1 (Preparation of dispersant 2-1C and preparation of slurry

using dispersant 2-1C)

Comparative Example 2-1 was performed similarly to Example 1-1 except that an aqueous solution of IPA at a concentration of 65% was supplied to the first flask at 8.0 g per minute instead of using the aqueous solution of IPA at a concentration of 35% in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 2-1C which contains an acryl-based polymer 2-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 2-1C in the same manner as those in Example 1-1.

[0088]

Comparative Example 2-2 (Preparation of dispersant 2-2C and preparation of slurry using dispersant 2-2C)

In this Comparative Example 2-2, a dispersant 2-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 2-1C in Comparative Example 2-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 2-1 was measured, the IPA concentration was 55%. The recovered IPA aqueous solution was concentrated to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 2-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 65%. The operation of Comparative Example 2-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 2-2C which contains an acryl-based polymer 2-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 2-2C in the same manner as those in Comparative Example 2-1.

[0089]

Comparative Example 3-1 (Preparation of dispersant 3-1C and preparation of slurry using dispersant 3-1C)

Comparative Example 3-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hypophosphite at a concentration of 30% to the first flask was 0.20 g per minute instead of 0.55 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 3-1C which contains an acryl-based polymer 3-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 3-1C in the same manner as those in Example 1-1.

[0090]

Comparative Example 3-2 (Preparation of dispersant 3-2C and preparation of slurry using dispersant 3-2C)

In this Comparative Example 3-2, a dispersant 3-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 3-1C in Comparative Example 3-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 3-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 3-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 3-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 3-2C which contains an acryl-based polymer 3-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 3-2C in the same manner as those in Comparative Example 3-1.

[0091]

Comparative Example 4-1 (Preparation of dispersant 4-1C and preparation of slurry using dispersant 4-1C)

Comparative Example 4-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hypophosphite at a concentration of 30% to the first flask was 0.90 g per minute instead of 0.55 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 4-1C which contains an acryl-based polymer 4-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 4-1C in the same manner as those in Example 1-1.

[0092]

Comparative Example 4-2 (Preparation of dispersant 4-2C and preparation of slurry using dispersant 4-2C)

In this Comparative Example 4-2, a dispersant 4-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 4-1C in

Comparative Example 4-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 4-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 4-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 4-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 4-2C which contains an acryl-based polymer 4-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 4-2C in the same manner as those in Comparative Example 4-1.

[0093]

Comparative Example 5-1 (Preparation of dispersant 5-1C and preparation of slurry using dispersant 5-1C)

Comparative Example 5-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hydroxide at a concentration of 48% to the first flask was 0.2 g per minute instead of 0.7 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 5-1C which contains an acryl-based polymer 5-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 5-1C in the same manner as those in Example 1-1.

[0094]

Comparative Example 5-2 (Preparation of dispersant 5-2C and preparation of slurry using dispersant 5-2C)

In this Comparative Example 5-2, a dispersant 5-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 5-1C in Comparative Example 5-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 5-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 5-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 5-1 was continued using the IPA aqueous solution whose concentration

was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 5-2C which contains an acryl-based polymer 5-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 5-2C in the same manner as those in Comparative Example 5-1.

[0095]

Comparative Example 6-1 (Preparation of dispersant 6-1C and preparation of slurry using dispersant 6-1C)

Comparative Example 6-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hydroxide at a concentration of 48% to the first flask was 2.5 g per minute instead of 0.7 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered. The liquid was in an uneven state of being separated into two layers, and a dispersant as a liquid with a uniform appearance was not obtained.

Although sodium hydroxide was not supplied to the third flask, the neutralization rate of the reaction liquid corresponds to 50 mol%.

[0096]

Comparative Example 6-2 (Preparation of dispersant 6-2C and preparation of slurry using dispersant 6-2C)

In this Comparative Example 6-2, a dispersant 6-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 6-1C in Comparative Example 6-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 6-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 6-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 6-1 was continued using the IPA aqueous solution whose concentration was adjusted. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered. The liquid was in an uneven state of being separated into two layers, and a dispersant as a liquid with a uniform appearance was not obtained.

Although sodium hydroxide was not supplied to the third flask, the neutralization rate of the reaction liquid corresponds to 50 mol%.

[0097]

Comparative Example 7-1 (Preparation of dispersant 7-1C and preparation of slurry

using dispersant 7-1C)

Comparative Example 7-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium persulfate at a concentration of 15% to the first flask was 0.10 g per minute instead of 0.30 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 7-1C which contains an acryl-based polymer 7-1C and has a solid content of 40% and pH of 4. A large amount of unreacted AA was left in the dispersant 7-1C.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 7-1C in the same manner as those in Example 1-1.

[0098]

Comparative Example 7-2 (Preparation of dispersant 7-2C and preparation of slurry using dispersant 7-2C)

In this Comparative Example 7-2, a dispersant 7-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 7-1C in Comparative Example 7-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 7-1 was measured, the IPA concentration was 40%. Inclusion of AA was confirmed in the recovered IPA aqueous solution. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 7-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 7-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 7-2C which contains an acryl-based polymer 7-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 7-2C in the same manner as those in Comparative Example 7-1.

[0099]

Comparative Example 8-1 (Preparation of dispersant 8-1C and preparation of slurry using dispersant 8-1C)

Comparative Example 8-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium persulfate at a concentration of 15% to the first flask was 0.80 g per minute instead of 0.30 g per minute in Example 1-1. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 8-1C which contains an acryl-based polymer 8-1C and has a solid content of 40%

and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 8-1C in the same manner as those in Example 1-1.

[0100]

Comparative Example 8-2 (Preparation of dispersant 8-2C and preparation of slurry using dispersant 8-2C)

In this Comparative Example 8-2, a dispersant 8-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 8-1C in Comparative Example 8-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 8-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 8-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 8-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 8-2C which contains an acryl-based polymer 8-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 8-2C in the same manner as those in Comparative Example 8-1.

[0101]

Comparative Example 9-1 (Preparation of dispersant 9-1C and preparation of slurry using dispersant 9-1C)

Comparative Example 9-1 was performed similarly to Example 1-1 except that temperatures (polymerization temperatures) held in the first, second, and third flasks in Example 1-1 were set to 60°C instead of 80°C. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 9-1C which contains an acryl-based polymer 9-1C and has a solid content of 40% and pH of 4. A large amount of unreacted AA was left in the dispersant 9-1C.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 9-1C in the same manner as those in Example 1-1.

[0102]

Comparative Example 9-2 (Preparation of dispersant 9-2C and preparation of slurry using dispersant 9-2C)

In this Comparative Example 9-2, a dispersant 9-2C was prepared using the aqueous

solution of IPA distilled off and recovered in the preparation of the dispersant 9-1C in Comparative Example 9-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 9-1 was measured, the IPA concentration was 40%. Inclusion of AA was confirmed in the recovered IPA aqueous solution. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 9-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 9-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 9-2C which contains an acryl-based polymer 9-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 9-2C in the same manner as those in Comparative Example 9-1.

[0103]

Comparative Example 10-1 (Preparation of dispersant 10-1C and preparation of slurry using dispersant 10-1C)

Comparative Example 10-1 was performed similarly to Example 1-1 except that temperatures (polymerization temperatures) held in the first, second, and third flasks in Example 1-1 were set to 89°C instead of 80°C. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 10-1C which contains an acryl-based polymer 10-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 10-1C in the same manner as those in Example 1-1.

[0104]

Comparative Example 10-2 (Preparation of dispersant 10-2C and preparation of slurry using dispersant 10-2C)

In this Comparative Example 10-2, a dispersant 10-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 10-1C in Comparative Example 10-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 10-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 10-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation

of Comparative Example 10-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 10-2C which contains an acryl-based polymer 10-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 10-2C in the same manner as those in Comparative Example 10-1.

[0105]

Comparative Example 11-1 (Preparation of dispersant 11-1C and preparation of slurry using dispersant 11-1C)

Comparative Example 11-1 was performed similarly to Example 1-1 except that the supply rate of the aqueous solution of sodium hydroxide at a concentration of 48% to the first flask was 0.6 g per minute instead of 0.7 g per minute in Example 1-1 and that the sodium hydroxide was not supplied into the third flask. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 11-1C which contains an acryl-based polymer 11-1C and has a solid content of 40% and pH of 2. Since the supply amount of the aqueous solution of sodium hydroxide was 0.6 g per minute and sodium hydroxide was not supplied into the third flask, as described above, the neutralization rate became 13 mol%.

The resulting dispersant 11-1C was used to perform wet grinding in the same manner as in Example 1-1. The viscosity of a slurry was high, and grinding could not be performed as expected.

[0106]

Comparative Example 11-2 (Preparation of dispersant 11-2C and preparation of slurry using dispersant 11-2C)

In this Comparative Example 11-2, a dispersant 11-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 11-1C in Comparative Example 11-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 11-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 11-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 11-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 11-2C which contains an

acryl-based polymer 11-2C and has a solid content of 40% and pH of 2. The neutralization rate in Comparative Example 11-2 was also 13 mol% as in Comparative Example 11-1.

The resulting dispersant 11-2C was used to perform wet grinding in the same manner as in Comparative Example 11-1. The viscosity of a slurry was high, and grinding could not be performed as expected.

[0107]

Comparative Example 12-1 (Preparation of dispersant 12-1C and preparation of slurry using dispersant 12-1C)

Comparative Example 12-1 was performed similarly to Example 1-1 except that the neutralization rate of the reaction liquid in the third flask by the aqueous solution of sodium hydroxide at a concentration of 48% in Example 1-1 was set to 98 mol% instead of 22 mol%. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 12-1C which contains an acryl-based polymer 12-1C and has a solid content of 40% and pH of 9.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 12-1C in the same manner as those in Example 1-1.

[0108]

Comparative Example 12-2 (Preparation of dispersant 12-2C and preparation of slurry using dispersant 12-2C)

In this Comparative Example 12-2, a dispersant 12-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 12-1C in Comparative Example 12-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 12-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 12-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 12-1 was continued using the IPA aqueous solution whose concentration was adjusted. Once the operation was continued for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 12-2C which contains an acryl-based polymer 12-2C and has a solid content of 40% and pH of 9.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 12-2C in the same manner as those in Comparative Example 12-1.

[0109]

Comparative Example 13-1 (Preparation of dispersant 13-1C and preparation of slurry

using dispersant 13-1C)

Regarding the supply of the aqueous solution of sodium hydroxide at a concentration of 48% into the first flask in Example 1-1, the aqueous solution of sodium hydroxide at a concentration of 48% was not supplied into the first flask in Comparative Example 13-1. Comparative Example 13-1 was performed as in Example 1-1 except for the above point. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 13-1C which contains an acryl-based polymer 13-1C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 13-1C in the same manner as those in Example 1-1.

[0110]

Comparative Example 13-2 (Preparation of dispersant 13-2C and preparation of slurry using dispersant 13-2C)

In this Comparative Example 13-2, a dispersant 13-2C was prepared using the aqueous solution of IPA distilled off and recovered in the preparation of the dispersant 13-1C in Comparative Example 13-1.

When the IPA concentration of the aqueous solution of IPA recovered in Comparative Example 13-1 was measured, the IPA concentration was 40%. Deionized water was added to set the same IPA concentration of an IPA aqueous solution as the IPA concentration of the IPA aqueous solution used in Comparative Example 13-1, and the IPA aqueous solution was obtained in the form of an aqueous solution of IPA at a concentration of 35%. The operation of Comparative Example 13-1 was continued using the IPA aqueous solution whose concentration was adjusted. After continuing the above operation for 20 hours, the liquid discharged from the third flask was recovered to obtain a dispersant 13-2C which contains an acryl-based polymer 13-2C and has a solid content of 40% and pH of 4.

After that, a ground calcium carbonate slurry was produced using the resulting dispersant 13-2C in the same manner as those in Comparative Example 13-1.

[0111]

Table 1-1

	Raw material used in the first flask and supply amount	Reaction condition	Example							
			1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2
Physicality/Evaluation	Acrylic acid (g/min.)		4.5			4.5				
	IPA concentration (%)		35			22				
	Aqueous solution of IPA (g/min.)		9.0			9.0				
	Number of parts of IPA based on 100 parts of monomer		70			44				
	Sodium hypophosphite concentration (%)		30			30				
	Sodium hypophosphite (g/min.)		0.55			0.55				
	Number of parts of sodium hypophosphite based on 100 parts of monomer		3.7			3.7				
	Sodium hydroxide concentration (%)		48			48				
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)		0.70			0.70				
	Number of parts of sodium hydroxide based on 100 parts of monomer		7.5			7.5				
	Sodium persulfate concentration (%)		15			15				
	Sodium persulfate aqueous solution (g/min.)		0.30			0.30				
Dispersant for wet grinding of calcium carbonate	Number of parts of sodium persulfate based on 100 parts of monomer		1.0			1.0				
	First flask: reaction temperature in polymerization process (°C)		80			80				
	First flask: mean residence time (min.)		90			90				
	Second flask: mean residence time (min.)		90			90				
	Thin film evaporator: distilling liquid containing IPA (g/min.)		7.9			5.0				
	Thin film evaporator: dilution water (g/min.)		4.9			2.0				
	Third flask: carboxyl group neutralization rate (mol%)		22			22				
	Dispersant for wet grinding of calcium carbonate		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2
	Solid content (% by mass)		40	40	40	40	40	40	40	40
	pH		4	4	4	4	4	4	4	4
	Weight-average molecular weight (Mw)		6200	6200	6600	6600	5600	5600	6100	6100
	<1.32-μm integrated value of slurry (%)		100	100	100	100	100	100	100	100
Physicality/Evaluation	Median diameter of slurry (μm)		0.67	0.67	0.68	0.68	0.66	0.66	0.67	0.67
	Slurry viscosity at current day of wet grinding (mPa·s)		210	210	220	220	200	200	200	200
	Slurry viscosity after 7 days (mPa·s)		2000	2000	1900	1900	2000	2000	1900	1900

Table 1-2

	Raw material used in the first flask and supply amount	Example						
		5-1	5-2	6-1	6-2	7-1	7-2	
Reaction condition	Acrylic acid (g/min.)		4.5		4.5		4.5	
	IPA concentration (%)		35		35		35	
	Aqueous solution of IPA (g/min.)		9.0		9.0		9.0	
	Number of parts of IPA based on 100 parts of monomer		70		70		70	
	Sodium hypophosphite concentration (%)		30		30		30	
	Sodium hypophosphite (g/min.)		0.55		0.55		0.55	
	Number of parts of sodium hypophosphite based on 100 parts of monomer		3.7		3.7		3.7	
	Sodium hydroxide concentration (%)		48		48		48	
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)		0.70		0.70		0.70	
	Number of parts of sodium hydroxide based on 100 parts of monomer		7.5		7.5		7.5	
	Sodium persulfate concentration (%)		15		15		15	
	Sodium persulfate aqueous solution (g/min.)		0.45		0.30		0.30	
	Number of parts of sodium persulfate based on 100 parts of monomer		1.5		1.0		1.0	
	First flask: reaction temperature in polymerization process (°C)		80		75		80	
Dispersant for wet grinding of calcium carbonate	First flask: mean residence time (min.)		90		90		90	
	Second flask: mean residence time (min.)		90		90		90	
	Thin film evaporator: distilling liquid containing IPA (g/min.)		7.9		7.9		7.9	
	Thin film evaporator: dilution water (g/min.)		4.8		4.9		4.6	
	Third flask: carboxyl group neutralization rate (mol%)		22		22		40	
	Dispersant for wet grinding of calcium carbonate	5-1	5-2	6-1	6-2	7-1	7-2	
	Solid content (% by mass)	40	40	40	40	40	40	
Physically/Evaluation	pH	4	4	4	4	5	5	
	Weight-average molecular weight (Mw)	5800	5800	6200	6300	6200	6200	
	<1.32- μ m integrated value of slurry (%)	100	100	100	100	100	100	
	Median diameter of slurry (μ m)	0.67	0.67	0.67	0.67	0.68	0.68	
	Slurry viscosity at current day of wet grinding (mPa·s)	200	200	210	210	230	230	
	Slurry viscosity after 7 days (mPa·s)	2100	2100	2000	2100	2400	2400	

Table 2-1

	Raw material used in the first flask and supply amount	Comparative Example					
		1-1	1-2	2-1	2-2	3-1	3-2
Reaction condition	Acrylic acid (g/min.)		4.5		4.5		4.5
	IPA concentration (%)		6.7		65		35
	Aqueous solution of IPA (g/min.)		9.0		8.0		9.0
	Number of parts of IPA based on 100 parts of monomer		13		116		70
	Sodium hypophosphite concentration (%)		30		30		30
	Sodium hypophosphite (g/min.)		0.55		0.55		0.20
	Number of parts of sodium hypophosphite based on 100 parts of monomer		3.7		3.7		1.3
	Sodium hydroxide concentration (%)		48		48		48
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)		0.70		0.70		0.70
	Number of parts of sodium hydroxide based on 100 parts of monomer		7.5		7.5		7.5
	Sodium persulfate concentration (%)		15		15		15
	Sodium persulfate aqueous solution (g/min.)		0.30		0.30		0.30
	Number of parts of sodium persulfate based on 100 parts of monomer		1.0		1.0		1.0
Physicality/Evaluation	First flask: reaction temperature in polymerization process (°C)		80		80		80
	First flask: mean residence time (min.)		90		90		90
	Second flask: mean residence time (min.)		90		90		90
	Thin film evaporator: distilling liquid containing IPA (g/min.)		3.0		10.4		7.9
	Thin film evaporator: dilution water (g/min.)		0.0		8.4		5.0
	Third flask: carboxyl group neutralization rate (mol%)		22		22		22
	Dispersant for wet grinding of calcium carbonate						
Physicality/Evaluation	Solid content (% by mass)	1-1C	1-2C	2-1C	2-2C	3-1C	3-2C
	pH	40	40	40	40	40	40
	Weight-average molecular weight (Mw)	4	4	4	4	4	4
	<1.32- μ m integrated value of slurry (%)	12000	12000	4300	4200	10000	11000
	Median diameter of slurry (μ m)	100	100	100	100	100	100
	Slurry viscosity at current day of wet grinding (mPa·s)	0.68	0.68	0.66	0.66	0.68	0.68
	Slurry viscosity after 7 days (mPa·s)	1500	1500	230	250	1100	1100
Remarks		7100	7200	7900	8100	6400	6300
		IPA is required to be concentrated.					

Table 2-2

	Raw material used in the first flask and supply amount	Comparative Example					
		4-1	4-2	5-1	5-2	6-1	6-2
Reaction condition	Acrylic acid (g/min.)		4.5		4.5		4.5
	IPA concentration (%)		35		35		35
	Aqueous solution of IPA (g/min.)		9.0		9.0		9.0
	Number of parts of IPA based on 100 parts of monomer		70		70		70
	Sodium hypophosphite concentration (%)		30		30		30
	Sodium hypophosphite (g/min.)		0.90		0.55		0.55
	Number of parts of sodium hypophosphite based on 100 parts of monomer		6.0		3.7		3.7
	Sodium hydroxide concentration (%)		48		48		48
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)		0.70		0.20		2.50
	Number of parts of sodium hydroxide based on 100 parts of monomer		7.5		2.1		26.7
	Sodium persulfate concentration (%)		15		15		15
	Sodium persulfate aqueous solution (g/min.)		0.30		0.30		0.30
	Number of parts of sodium persulfate based on 100 parts of monomer		1.0		1.0		1.0
	First flask: reaction temperature in polymerization process (°C)		80		80		80
	First flask: mean residence time (min.)		90		90		90
	Second flask: mean residence time (min.)		90		90		90
Physicality/Evaluation	Thin film evaporator: distilling liquid containing IPA (g/min.)		7.9		7.9		7.9
	Thin film evaporator: dilution water (g/min.)		4.8		4.9		4.4
	Third flask: carboxyl group neutralization rate (mol%)		22		22		50
	Dispersant for wet grinding of calcium carbonate	4-1C	4-2C	5-1C	5-2C	6-1C	6-2C
	Solid content (% by mass)	40	40	40	40	-	-
	pH	4	4	4	4	-	-
	Weight-average molecular weight (Mw)	4300	4200	6200	6200	-	-
	<1.32- μ m integrated value of slurry (%)	100	100	100	100	-	-
	Median diameter of slurry (μ m)	0.66	0.66	0.67	0.67	-	-
	Slurry viscosity at current day of wet grinding (mPa·s)	1000	1100	1000	1000	-	-
Slurry viscosity after 7 days (mPa·s)		8000	8200	6900	6900	-	-
Remarks						Uniform liquid could not be obtained in 6-1 and 6-2.	

Table 3-1

	7-1	7-2	Comparative Example			
			8-1	8-2	9-1	9-2
Raw material used in the first flask and supply amount	Acrylic acid (g/min.)	4.5		4.5		4.5
	IPA concentration (%)	35		35		35
	Aqueous solution of IPA (g/min.)	9.0		9.0		9.0
	Number of parts of IPA based on 100 parts of monomer	70		70		70
	Sodium hypophosphite concentration (%)	30		30		30
	Sodium hypophosphite (g/min.)	0.55		0.55		0.55
	Number of parts of sodium hypophosphite based on 100 parts of monomer	3.7		3.7		3.7
	Sodium hydroxide concentration (%)	48		48		48
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)	0.70		0.70		0.70
	Number of parts of sodium hydroxide based on 100 parts of monomer	7.5		7.5		7.5
	Sodium persulfate concentration (%)	15		15		15
	Sodium persulfate aqueous solution (g/min.)	0.10		0.80		0.30
	Number of parts of sodium persulfate based on 100 parts of monomer	0.3		2.7		1.0
Reaction condition	First flask: reaction temperature in polymerization process (°C)	80		80		60
	First flask: mean residence time (min.)	90		90		90
	Second flask: mean residence time (min.)	90		90		90
	Thin film evaporator: distilling liquid containing IPA (g/min.)	7.9		7.9		7.9
	Thin film evaporator: dilution water (g/min.)	5.0		4.6		4.9
	Third flask: carboxyl group neutralization rate (mol%)	22		22		22
Dispersant for wet grinding of calcium carbonate		7-1C	7-2C	8-1C	8-2C	9-1C
	Solid content (% by mass)	40	40	40	40	40
	pH	4	4	4	4	4
Physicality/Evaluation	Weight-average molecular weight (Mw)	9300	9500	4900	4800	8600
	<1.32- μ m integrated value of slurry (%)	100	100	100	100	100
	Median diameter of slurry (μ m)	0.68	0.68	0.67	0.67	0.68
	Slurry viscosity at current day of wet grinding (mPa·s)	1000	1200	900	900	1100
	Slurry viscosity after 7 days (mPa·s)	7500	8000	6600	6700	8400
Remarks	Amount of unreacted AA was large.		AA was included in IPA.		Amount of unreacted AA was large. AA was included in IPA.	

Table 3-2

	Raw material used in the first flask and supply amount	Comparative Example					
		10-1	10-2	11-1	11-2	12-1	12-2
Reaction condition	Acrylic acid (g/min.)		4.5		4.5		4.5
	IPA concentration (%)		35		35		35
	Aqueous solution of IPA (g/min.)		9.0		9.0		9.0
	Number of parts of IPA based on 100 parts of monomer		70		70		70
	Sodium hypophosphite concentration (%)		30		30		30
	Sodium hypophosphite (g/min.)		0.55		0.55		0.55
	Number of parts of sodium hypophosphite based on 100 parts of monomer		3.7		3.7		3.7
	Sodium hydroxide concentration (%)		48		48		48
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)		0.70		0.60		0.70
	Number of parts of sodium hydroxide based on 100 parts of monomer		7.5		6.4		7.5
Physicality/Evaluation	Sodium persulfate concentration (%)		15		15		15
	Sodium persulfate aqueous solution (g/min.)		0.30		0.30		0.30
	Number of parts of sodium persulfate based on 100 parts of monomer		1.0		1.0		1.0
	First flask: reaction temperature in polymerization process (°C)		89		80		80
	First flask: mean residence time (min.)		90		90		90
	Second flask: mean residence time (min.)		90		90		90
	Thin film evaporator: distilling liquid containing IPA (g/min.)		7.9		7.9		7.9
	Thin film evaporator: dilution water (g/min.)		4.9		5.0		3.5
	Third flask: carboxyl group neutralization rate (mol%)		22		13		98
	Dispersant for wet grinding of calcium carbonate	10-1C	10-2C	11-1C	11-2C	12-1C	12-2C
Physicality/Evaluation	Solid content (% by mass)	40	40	40	40	40	40
	pH	4	4	2	2	9	9
	Weight-average molecular weight (Mw)	5700	5700	6200	6200	6200	6200
	<1.32- μ m integrated value of slurry (%)	100	100	-	-	100	100
	Median diameter of slurry (μ m)	0.67	0.67	-	-	0.68	0.68
	Slurry viscosity at current day of wet grinding (mPa·s)	1100	1100	-	-	1000	1000
	Slurry viscosity after 7 days (mPa·s)	7200	7200	-	-	9000	9000
Remarks		Grinding could not be performed in 11-1 and 11-2.					

Table 4

		Comparative Example	
		13-1	13-2
Raw material used in the first flask and supply amount	Acrylic acid (g/min.)	4.5	
	IPA concentration (%)	35	
	Aqueous solution of IPA (g/min.)	9.0	
	Number of parts of IPA based on 100 parts of monomer	70	
	Sodium hypophosphite concentration (%)	30	
	Sodium hypophosphite (g/min.)	0.55	
	Number of parts of sodium hypophosphite based on 100 parts of monomer	3.7	
	Sodium hydroxide concentration (%)	not used	
	Aqueous solution of sodium hydroxide aqueous solution (g/min.)	0.00	
	Number of parts of sodium hydroxide based on 100 parts of monomer	0.0	
	Sodium persulfate concentration (%)	15	
	Sodium persulfate aqueous solution (g/min.)	0.30	
	Number of parts of sodium persulfate based on 100 parts of monomer	1.0	
Reaction condition	First flask: reaction temperature in polymerization process (°C)	80	
	First flask: mean residence time (min.)	90	
	Second flask: mean residence time (min.)	90	
	Thin film evaporator: distilling liquid containing IPA (g/min.)	7.9	
	Thin film evaporator: dilution water (g/min.)	4.9	
	Third flask: carboxyl group neutralization rate (mol%)	22	
Dispersant for wet grinding of calcium carbonate		13-1C	13-2C
Physicality/Evaluation	Solid content (% by mass)	40	40
	pH	4	4
	Weight-average molecular weight (Mw)	6500	6500
	<1.32- μ m integrated value of slurry (%)	100	100
	Median diameter of slurry (μ m)	0.67	0.67
	Slurry viscosity at current day of wet grinding (mPa·s)	1000	1000
	Slurry viscosity after 7 days (mPa·s)	7800	7800

[0115]

In Examples 1-1 to 7-2, usage amounts of isopropyl alcohol, sodium hypophosphite, sodium persulfate, and sodium hydroxide were respectively in the range from 15 to 100 parts, 2.0 to 5.0 parts, 0.5 to 2.0 parts, and 5.0 to 20 parts based on 100 parts of a monomer, the reaction temperature in the polymerization process was in the range from 68°C to 82°C, and the neutralization rate of carboxyl groups was 15 to 95 mol%. According to the above results, it was found that dispersants of Examples 1-1 to 7-2 were ones in which an initial viscosity of a calcium carbonate slurry obtained by wet grinding was low, and a significant increase in the viscosity with passage of time was suppressed.

Meanwhile, in Comparative Examples 1-1 and 1-2, usage amount of IPA was so small as 13 parts based on 100 parts of the monomer. The weight-average molecular weight of the resulting acryl-based polymer contained in the dispersant was 12,000 and was larger than a preferable range (4,500 to 8,500). According to those facts, when the dispersants of Comparative Examples 1-1 and 1-2 were used, slurry viscosities at the time of grinding of

calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

In Comparative Examples 2-1 and 2-2, slurry viscosities at the time of grinding of calcium carbonate were low. However, since usage amount of IPA was so large as 116 parts based on 100 parts of the monomer, the weight-average molecular weights of the resulting acryl-based polymers contained in the dispersants were approximately 4,300 and were smaller than a preferable range. Thus, a significant increase was observed in slurry viscosities after seven days. Additionally, the concentrations of IPA in the aqueous solutions of IPA used in Comparative Examples 2-1 and 2-2 were so high as 65%, and therefore, when the recovered IPA was reused, the recovered IPA aqueous solution (azeotrope) was required to be concentrated.

[0116]

In Comparative Examples 3-1 and 3-2, usage amount of sodium hypophosphite was so small as 1.3 parts based on 100 parts of the monomer, and the weight-average molecular weights of the resulting acryl-based polymers were slightly large to be approximately 10,000. According to those facts, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

In Comparative Examples 4-1 and 4-2, since usage amount of sodium hypophosphite was so large as 6.0 parts based on 100 parts of the monomer, weight-average molecular weights of the resulting acryl-based polymers were smaller than a preferable range. However, since usage amount of sodium hypophosphite was large, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

[0117]

In Comparative Examples 5-1 and 5-2, weight-average molecular weights of the resulting acryl-based polymers were within a preferred range. Since usage amount of sodium hydroxide was so small as 2.1 parts based on 100 parts of the monomer, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in the slurry viscosities after seven days.

In Comparative Examples 6-1 and 6-2, since usage amount of sodium hydroxide was so large as 26.7 parts based on 100 parts of the monomer, the obtained reaction liquids (dispersants) were in an uneven state of being separated into two layers and could not be used as a dispersant.

[0118]

In Comparative Examples 7-1 and 7-2, since usage amount of sodium persulfate was

so small as 0.3 part based on 100 parts of the monomer, weight-average molecular weights of the resulting acryl-based polymers were slightly large to be approximately 9,300. Moreover, the amount of unreacted acrylic acid was large, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days. The inclusion of the unreacted acrylic acid was observed in the recovered IPA aqueous solution in Comparative Example 7-1 used in Comparative Example 7-2.

In Comparative Examples 8-1 and 8-2, since usage amount of sodium persulfate was so large as 2.7 parts based on 100 parts of the monomer, weight-average molecular weights of the resulting acryl-based polymers were within a preferred range. However, since usage amount of sodium persulfate was large, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

[0119]

In Comparative Examples 9-1 and 9-2, since the reaction temperature in the polymerization process was so low as 60°C, weight-average molecular weights of the resulting acryl-based polymers were slightly large. Moreover, the amount of unreacted acrylic acid was large, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days. The inclusion of the unreacted acrylic acid was observed in the recovered IPA aqueous solution in Comparative Example 9-1 used in Comparative Example 9-2.

In Comparative Examples 10-1 and 10-2, weight-average molecular weights of the resulting acryl-based polymers were within a preferred range. Since the reaction temperature in the polymerization process was so high as 89°C, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

[0120]

In Comparative Examples 11-1 and 11-2, since neutralization rates of carboxyl groups were so low as 13 mol%, viscosities of the obtained slurry were high and calcium carbonate could not be ground.

In Comparative Examples 12-1 and 12-2, calcium carbonate could be ground. However, since neutralization rates of carboxyl groups were so high as 98 mol%, slurry viscosities at the time of grinding of calcium carbonate were high, and a significant increase was observed in slurry viscosities after seven days.

In Comparative Examples 13-1 and 13-2, since sodium hydroxide was not used in the polymerization process, slurry viscosities at the time of grinding of calcium carbonate were high,

and a significant increase was observed in slurry viscosities after seven days. It is considered that this was because the oxidation reaction of sodium hypophosphite in the polymerization process was not suppressed.

[INDUSTRIAL APPLICABILITY]

[0121]

Clearly from the above description, the dispersion for calcium carbonate of the present invention exhibits excellent dispersibility and long-term dispersion stability. In particular, the dispersion is effectively used as a dispersant for wet grinding of calcium carbonate.

According to the production method of a dispersant for calcium carbonate of the present invention, the above dispersant for calcium carbonate can be efficiently produced. When the recovered isopropyl alcohol from the concentration process according to the present invention is used in the polymerization process, evaporated isopropyl alcohol need not be disposed of. Therefore, it is possible to provide a method for producing a dispersant for calcium carbonate that can reduce cost, and achieve excellent production efficiency and environmental protection.

What is claimed is:

1. A dispersant for calcium carbonate obtained by a method comprising sequentially a polymerization process and a neutralization process, characterized in that said polymerization process is a process in which a monomer containing acrylic acid, an isopropyl alcohol aqueous solution, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and said monomer is continuously polymerized, that a supply amount of isopropyl alcohol in said isopropyl alcohol aqueous solution is in the range from 15 to 100 parts by mass based on 100 parts by mass of said monomer, that a supply amount of said hypophosphite is in the range from 2.0 to 5.0 parts by mass based on 100 parts by mass of said monomer, that a supply amount of said persulfate is in the range from 0.5 to 2.0 parts by mass based on 100 parts by mass of said monomer, that a supply amount of said sodium hydroxide is in the range from 5.0 to 20 parts by mass based on 100 parts by mass of said monomer, that a reaction temperature in the polymerization process is between 68°C and 82°C, and that said neutralization process is a process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from said monomer constituting a polymer obtained in said polymerization process is neutralized.

2. The dispersant for calcium carbonate according to Claim 1,
wherein said method further comprises, between said polymerization process and said neutralization process, a concentration process in which said isopropyl alcohol is distilled off.

3. The dispersant for calcium carbonate according to Claim 2,
wherein said isopropyl alcohol recovered after said concentration process is used in said polymerization process.

4. The dispersant for calcium carbonate according to any one of Claims 1 to 3,
wherein a concentration of said isopropyl alcohol in said isopropyl alcohol aqueous solution is in the range from 15% to 55% by mass.

5. The dispersant for calcium carbonate according to any one of Claims 1 to 4,
wherein a content of said acrylic acid in said monomer is in the range from 80% to 100% by mass based on 100% by mass of a total amount of said monomer.

6. A continuous production method of the dispersant for calcium carbonate according to Claim 1, characterized in that said method comprises a polymerization process and a neutralization process sequentially,

wherein said polymerization process is a process in which a monomer containing acrylic acid, an isopropyl alcohol aqueous solution, a hypophosphite, a persulfate, and sodium hydroxide are continuously supplied to a reactor, and said monomer is continuously

polymerized,

wherein a supply amount of isopropyl alcohol in said isopropyl alcohol aqueous solution is in the range from 15 to 100 parts by mass based on 100 parts by mass of said monomer,

wherein a supply amount of said hypophosphite is in the range from 2.0 to 5.0 parts by mass based on 100 parts by mass of said monomer,

wherein a supply amount of said persulfate is in the range from 0.5 to 2.0 parts by mass based on 100 parts by mass of said monomer,

wherein a supply amount of said sodium hydroxide is in the range from 5.0 to 20 parts by mass based on 100 parts by mass of said monomer,

wherein a reaction temperature in the polymerization process is between 68°C and 82°C, and

wherein said neutralization process is a process in which 15 to 95 mol% of carboxyl groups included in a structural unit derived from said monomer constituting a polymer obtained in said polymerization process is neutralized.

7. The continuous production method of the dispersant for calcium carbonate according to Claim 6,

wherein said polymerization process is performed so that two or more continuous vessel-type reactors are installed in series.

8. The continuous production method of the dispersant for calcium carbonate according to Claim 6 or 7,

wherein said method further comprises, between said polymerization process and said neutralization process, a concentration process in which said isopropyl alcohol is distilled off.

9. The continuous production method of the dispersant for calcium carbonate according to Claim 8,

wherein a thin film evaporator is used in said concentration process.

10. The continuous production method of the dispersant for calcium carbonate according to Claim 8 or 9,

wherein said isopropyl alcohol recovered after said concentration process is used in said polymerization process.

11. The continuous production method of the dispersant for calcium carbonate according to any one of Claims 6 to 10,

wherein a concentration of said isopropyl alcohol in said isopropyl alcohol aqueous solution is in the range from 15% to 55% by mass.

12. The continuous production method of the dispersant for calcium carbonate

according to any one of Claims 6 to 11,

wherein a content of said acrylic acid in said monomer is in the range from 80% to 100% by mass based on 100% by mass of a total amount of said monomer.