

SPECIFICATION

DISPERSANT FOR PIGMENT AND USE THEREOF

[FIELD OF THE INVENTION]

[0001]

The present invention relates to dispersant for pigment or various inorganic particles. More specifically, the present invention provides dispersant for dispersant including a (meth)acrylic acid-based (co)polymer which is preferably dispersant for calcium carbonate, which has high dispersion stabilizing effect, and is able to disperse in fine particle while keeping good fluidity especially when used for producing a high concentrated pigment slurry with a solid content greater than 70% by mass or dispersant slurry having extremely small particle sizes, and which is able to stably disperse while suppressing viscosity increase and pH lowering of the slurry with age for a long time.

[BACKGROUND ART]

[0002]

Homopolymer of acrylic acid (or acrylic acid salt) and copolymer formed from acrylic acid (salts) and other copolymerizable monomers have been known as a dispersant for stably dispersing inorganic pigment such as calcium carbonate, kaolin, satin white, talc, and the like in water.

In Patent literature 1 (JP-A S54-82416), a dispersant is dispersed with dispersant consisting of polycarboxylic acid (salt). In Patent Literature 2 (JP-A S49-130915), a dispersant is dispersed with dispersant consisting copolymer of carboxylic-acid-(salt)-containing monomer and (meth)acrylic acid ester monomer having 1 to 4 carbon atoms. In Patent Literature 3 (JP-A 2005-307023), a dispersant is dispersed with dispersant consisting of copolymer which is obtained using monomer containing carboxylic acid (salt) and other monomer, and which has at least one functional group derived from alcohol having 1 to 3 carbon atoms as a part of the end group in the copolymer.

[0003]

However, dispersion process with higher concentration and finer

particle dispersion process have been desired in recent years than in the past and there are more demands for suppressing viscosity increase of slurry containing inorganic pigment with age than ever before.

Inorganic and other pigments having small particle sizes in particular have large surface areas and thus have strong interaction between the particles, resulting in increasing occurrence of aggregation of particles, which makes these pigments tend to show increase in the slurry viscosity.

In addition, the pH of slurry obtained in aqueous systems has to be kept high because unwanted bacteria are more likely to grow in the neutral or lower pH range and may decompose the slurry, reducing their commercial values.

[0004]

The above-mentioned dispersants are yet to achieve a satisfactory level of performance with regard to these demands. It is hard to say that the dispersant consisting of polycarboxylic acid (salt) in Patent Literature 1 and the dispersant consisting of copolymer of carboxylic-acid-(salt)-containing monomer and (meth)acrylic acid ester monomer having 1 to 4 carbon atoms in Patent Literature 2 sufficiently suppress viscosity increase of dispersion liquids with age. In case of the inorganic pigment dispersant described in Patent Literature 3, since no specific optimization has been attempted for the resin structural units or neutralizing agents, it is hard to say that the dispersant is fully suitable for stabilizing dispersion liquids as inorganic pigment dispersant. Besides, there is no mention of pH.

[PRIOR ART LITERATURE]

[PATENT LITERATURE]

[0005]

Patent Literature 1: JP-A S54-82416

Patent Literature 2: JP-A S49-130915

Patent Literature 3: JP-A 2005-307023

[SUMMARY OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0006]

The object of the present invention is to provide dispersant excellent in stabilizing dispersion property for slurry containing inorganic pigment with small particle sizes at higher concentration with age, and in pH lowering suppressing effect of the slurry in higher pH range, which is required for the recent dispersant.

[MEANS FOR SOLVING THE PROBLEMS]

[0007]

The present inventors have wholeheartedly studied to solve the above-mentioned problems and surprisingly found that when the dispersant comprising the following constituents is used for dispersing of inorganic pigment, particularly calcium carbonate, it is not only capable of keeping dispersion liquid slurry within the high alkaline range despite the pH of the dispersant itself being low, but also provides advantages in stability, fluidity and filterability of the slurry with age.

[0008]

The first aspect of the present invention is a dispersant for inorganic pigment having pH of 6.0 or lower and is characterized in that the dispersant is a partially neutralized product of (A) polymer of (a) α,β -unsaturated carboxylic acid or (B) copolymer consisting of 80% to 99% by mole of a unit derived from (a) α,β -unsaturated carboxylic acid and 1% to 20% by mole of at least one unit selected from the group consisting of a unit derived from (b) (meth)acrylic acid ester and a unit derived from (c) (meth)acrylic acid ester of polyalkylene glycol, based on 100% by mole of the total of (a), (b) and (c), and that 20% to 80% by mole of the acid group is partially neutralized with ammonia or organic amine.

The second aspect of the present invention is a dispersant for pigment according to the first aspect, wherein the inorganic pigment is of calcium carbonate.

The third aspect of the present invention is a dispersant for calcium carbonate according to the second aspect, wherein the monomer (b) for forming the copolymer (B) is (meth)acrylic acid ester with 1 to 8 carbon atoms, and the monomer (c) is (meth)acrylic acid ester of polyalkylene glycol represented by the following general formula (1):



wherein R^1 is hydrogen atom or methyl group, R^2 is ethylene group or propylene group, R^3 is hydrogen atom or alkyl group with 1 to 6 carbon atoms, m is the number of 0 to 4, and n is the number of 2 to 10.

The fourth aspect of the present invention is a dispersant for calcium carbonate according to the second or third aspect, wherein the acid group in the unit derived from the monomer (a) in the polymer (A) or the copolymer (B) is in a form of organic amine salt.

The fifth aspect of the present invention is a dispersant for calcium carbonate according to any one of the second to fourth aspect, wherein the weight average molecular weight (Mw) of the polymer (A) or the copolymer (B) is in the range from 4,000 to 8,000 based on polyacrylic acid standard by gel permeation chromatography, and Mw/Mn (weight average molecular weight/number average molecular weight) is 2.7 or less.

The sixth aspect of the present invention is a dispersant for calcium carbonate according to any one of the second to fifth aspect, wherein the dispersant is of the copolymer (B).

The seventh aspect of the present invention is a dispersant for calcium carbonate according to any one of the second to sixth aspect, wherein the monomer (a) for forming the copolymer (B) is acrylic acid, the monomer (b) is butyl acrylate, and the monomer (c) is polypropylene glycol mono (meth)acrylate where R^2 in the general formula (1) is propylene group.

The eighth aspect of the present invention is a dispersant for calcium carbonate according to any one of the second to seventh aspect, wherein the organic amine is monoethanol amine.

The ninth aspect of the present invention is a dispersion liquid of calcium carbonate having pH of 9.5 or higher, which is prepared by wet grinding using the dispersant for calcium carbonate according to any one of the second to eighth aspect by wet grinding.

The tenth aspect of the present invention is a dispersion liquid of calcium carbonate according to the ninth aspect, wherein the calcium carbonate is ground calcium carbonate.

[EFFECT OF THE INVENTION]

[0009]

The (meth)acrylic acid (salt)-based (co)polymer according to the present invention is mainly used as dispersant for inorganic pigment such as calcium carbonate, kaolin, satin white, titanium oxide, talc, calcium phosphate, cement, gypsum, and the like. Particularly when the polymer is used for calcium carbonate, effects are obtained.

When a dispersion liquid of calcium carbonate is prepared using dispersant for calcium carbonate consisting of the (meth)acrylic acid (salt)-based (co)polymer according to the present invention, even if the concentration of calcium carbonate is high or the size of calcium carbonate particle is extremely small, the viscosity of the calcium carbonate dispersion liquid is low and excellent handling properties can be obtained. The viscosity increase of the dispersion liquid with age is never caused and the dispersion liquid is capable of maintaining a long-term low viscosity. Moreover, calcium carbonate dispersion liquid having excellent stability with age can be obtained free from particle aggregation.

When dispersion liquid of calcium carbonate is prepared using dispersant for calcium carbonate consisting of the (meth)acrylic acid (salt)-based (co)polymer of the present invention, in addition to low-viscosity dispersion liquid as described above, dispersion liquid having excellent handling properties in terms of fluidity, filterability and the like can also be obtained. Moreover, the dispersant is useful because it can keep the pH of the dispersion liquid of calcium carbonate within the strong alkaline range where the growth of bacteria can be inhibited.

Taking advantage of the above-mentioned characterization, the dispersant for calcium carbonate of the present invention can be effectively used as dispersing stabilizer of calcium carbonate for papermaking industry as well as for applications in plastics, rubbers, paints, inks, adhesives, sealants and the like.

[DESCRIPTION OF THE PREFERRED EMBODIMENTS]

[0010]

Hereinafter, the embodiments of the present invention are described in detail.

In the present invention, examples of the α,β -unsaturated carboxylic acid (a) include (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, and the like. Half-esterified product of phthalic anhydride or itaconic anhydride with alkyl alcohol may also be used. These compounds may be used singly or in combination of two or more types thereof.

Among these, (meth)acrylic acid is preferred. The (meth)acrylic acid according to the present invention refers to acrylic acid or methacrylic acid. Acrylic acid is more preferable for the stability of slurry and the ease of polymerization.

[0011]

The (meth)acrylic acid ester monomer (b) according to the present invention include linear, branched, or cyclic (meth)acrylic acid alkyl ester with alkyl group having 1 to 20 carbon atoms. Example thereof includes methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, and the like.

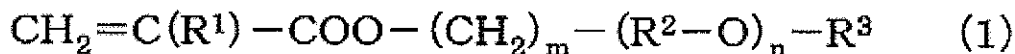
Additionally, hydroxyalkyl (meth)acrylate may be used including 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, ω -hydroxypolyalkylene glycol ($n = 2$ to 30) (meth)acrylate, and the like.

Further, (meth)acrylic acid ester containing sulfonate or phosphate group may be used including 3-sulfopropyl (meth)acrylate, mono(2-hydroxyethylacrylate) acid phosphate, mono(2-hydroxyethylmethacrylate) acid phosphate, mono(2-hydroxypropylacrylate) acid phosphate, mono(3-hydroxyethylacrylate) acid phosphate, mono(3-hydroxyethylmethacrylate) acid phosphate, and the like.

From the viewpoints of dispersibility of calcium carbonate and stability of the slurry, (meth)acrylic acid alkyl ester having 1 to 8 carbon atoms is preferable, and more preferable is butyl acrylate.

[0012]

The (meth)acrylic acid ester of polyalkylene glycol (c) is preferably one represented by the following general formula (1).



(In the formula, R^1 is hydrogen atom or methyl group, R^2 is ethylene group or propylene group, R^3 is hydrogen atom or alkyl group with 1 to 6 carbon atoms, m is the number of 0 to 4, and n is the number of 2 to 10)

Molecular weight of the polyalkylene glycol chain is preferably in the range from 100 to 2,000, and more preferable is polypropylene glycol mono(meth)acrylate in which R^2 in the general formula (1) is propylene group.

[0013]

Other monomers may also be copolymerized as long as the properties of the copolymer are not impaired in the present invention. Such monomer is not particularly limited. Example thereof includes amide-containing ethylenic unsaturated monomer such as (meth)acrylamide, N-methylol (meth)acrylamide, and the like; aromatic ethylenic unsaturated monomer such as styrene-based compound including styrene, α -methyl styrene, vinyl toluene, hydroxy styrene, and the like, and vinyl naphthalene-based compound; monomer having sulfonate group such as (meth)allyl sulfonate, styrene sulfonate, α -methyl styrene sulfonate, isoprene sulfonate, vinyl toluene sulfonate, (meth)allyloxy benzene sulfonate, (meth)allyloxy 2-hydroxypropyl sulfonate, bis(3-sulfopropyl) itaconate, and the like; and the like.

[0014]

For the dispersant of the present invention, polymer (A) formed from the monomer (a) or copolymer (B) formed from the monomers (a), and monomer (b) and/or monomer (c) can be used. The copolymer (B) is consisting of 80% to 99% by mole of the (a) and 1% to 20% by mole of the (b) and/or the (c) based on 100% by mole of the total of the (a), (b), and (c). From the viewpoints of a balance between the dispersibility of calcium carbonate and the stability, fluidity and filterability of slurry, the copolymer (B) is preferred. In the copolymer (B), if the content of the (b) and/or (c) is less than 1% by mole, the above-mentioned balance cannot be obtained and if it exceeds 80% by mole, the stability of the

slurry is insufficient in high pH range.

[0015]

The production methods of the polymer (A) and the copolymer (B) according to the present invention are not particularly limited and any of solution polymerization, emulsion polymerization and suspension polymerization may be used. Among these, solution polymerization is preferred.

Examples of solvent for solution polymerization include water; alcohol such as methanol ethanol, isopropanol, and the like; ketone such as acetone, methyl ethyl ketone, and the like; ether such as tetrahydrofuran, and the like; aliphatic hydrocarbon such as hexane, heptane, and the like; aromatic hydrocarbon such as toluene, xylene, and the like; mixture of these compounds; and the like. Among these, mixed solvent of alcohol and water is preferable. The more preferable is mixed solvent of isopropanol and water.

In the mixed solvent of the alcohol and water, the mixing ratio by weight of the alcohol to water is preferably in the range from 90:10 to 10:90, and more preferably from 70:30 to 30:70. If the content ratio of water exceeds 90% by mass, some of the monomer (b) and/or (c) will not be readily dissolved, being unfavorable. On the other hand, if the content ratio of water is less than 10% by mass, the alcohol needs to be substituted with water when the resulting mixture is used as dispersant, which requires additional cost and effort.

[0016]

As radical polymerization initiator for the production of the polymer (A) and copolymer (B) according to the present invention, peroxide radical polymerization initiator commonly used can be used. Example thereof includes water-soluble peroxide containing persulfate such as sodium persulfate, potassium persulfate, ammonium persulfate, and the like; hydroperoxide such as t-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, p-mentane hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, and the like; and hydrogen peroxide: and oil-soluble peroxide containing ketone peroxide such as methyl ethyl ketone peroxide, and cyclohexanone peroxide; dialkyl peroxide such as di-t-butyl peroxide,

t-butyl cumyl peroxide, dicumyl peroxide, α,α' -bis(t-butylperoxy)-p-diisopropylbenzene, α,α' -bis(t-butylperoxy)-n-diisopropylhexyne, and the like; peroxyester such as t-butylperoxy acetate, t-butylperoxy laurate, t-butylperoxy benzoate, di-t-butylperoxy isophthalate, 2,5-dimethyl-2,5-di(benzoyl peroxy)hexane, t-butylperoxy isopropyl carbonate, and the like; peroxy ketal such as n-butyl-4,4-bis(t-butylperoxy) valerate, 2,2-bis(t-butylperoxy)butane, and the like; diacyl peroxide such as dibenzoyl peroxide, and the like; and the like.

The above-mentioned radical polymerization initiator based on peroxide may be used singly or in combination of two or more types thereof. Among the above-mentioned peroxide radical polymerization initiators, hydrogen peroxide and persulfate are preferably used which facilitate the control of molecular weight and have low decomposition temperature.

[0017]

The amount of radical polymerization initiator used is not particularly limited. The usage amount is preferably in the range from 0.10% to 15% by mass, and particularly from 0.1% to 5% by mass based on the total mass of all monomers used for the production of the polymer (A) or the copolymer (B). If the usage amount of the radical polymerization initiator is too small, the conversion of polymerization tends to be reduced. On the other hand, if the usage amount thereof is excessive, the polymerization initiator may be left inside the polymer (A) or the copolymer (B) even after polymerization, to reduce stability or lead adverse effects on the performance as dispersant.

[0018]

When the polymer (A) or the copolymer (B) is produced, an appropriate amount of chain transfer agent may be added to the polymerization system in order to adjust the molecular weight. Examples of the chain transfer agent capable of using include sodium phosphite, sodium hypophosphite, sodium bisulfite, mercaptoacetic acid, mercaptopropionic acid, 2-propanethiol, 2-mercaptoethanol, thiophenol, dodecyl mercaptan, thioglycerol, thiomalic acid, and the like.

[0019]

The polymerization temperature for the production of the polymer (A) or the copolymer (B) is preferably in the range from 50°C to 150°C, and more preferably from 70°C to 100°C. If the polymerization temperature is below 50°C, the conversion of copolymerization tends to be decreased. On the other hand, if the polymerization temperature is higher than 150°C, the monomer (a) may undergo dimerization reaction or the monomer (b) or (c) may be thermally decomposed. Even the produced polymer (A) or copolymer (B) may also be thermally decomposed.

The polymerization time is preferably in the range from 3 to 20 hours, and particularly from 3 to 10 hours.

[0020]

It is preferable to carry out the polymerization reaction for producing the polymer (A) or the copolymer (B) at an unneutralized ratio of at least 40% by mole, more preferably 70% to 100% by mole, and particularly 90% to 100% by mole, in terms of the acid groups in the monomers (a) prior to and during polymerization in order to make the polymerization reaction proceed homogeneously.

[0021]

The polymer (A) and the copolymer (B) have weight-average molecular weight (M_w) (as measured by Gel Permeation Chromatography with polyacrylic acid as the standard substance) of usually 2,000 to 10,000, and preferably 4,000 to 8,000. If the weight-average molecular weight (M_w) is less than 2,000, the absorbability to calcium carbonate with age is reduced. On the other hand, if M_w is more than 10,000, the calcium carbonate particles are bonded (crosslinked) and the viscosity increase of the calcium carbonate slurry with age is caused.

The molecular weight distribution (M_w/M_n) which is a ratio of M_w to M_n is preferably 2.7 or less, more preferably 2.5 or less, and particularly 2.4 or less. If M_w/M_n is more than 2.7, the content of low-molecular-weight components having low absorbability to calcium carbonate with age is increased and the content of high-molecular-weight components which cause bonding (crosslinking) of the calcium carbonate particles is increased, and the viscosity increase of the calcium carbonate slurry with age is easily caused, being unfavorable.

[0022]

The (meth)acrylic (co)polymer salts according to the present invention can be obtained by the following method. After removal of the organic solvent from the solution containing the polymer (A) or the copolymer (B) obtained in the above procedure by distillation, vacuum distillation, drying or other operations as necessary, the carboxylic group in the unit from the monomer (a) from the polymer (A) or the copolymer (B) are neutralized with basic compound and are converted into the form of a salt which is water-soluble.

The basic compound for neutralization is ammonia or organic amine.

The neutralization is performed with at least one basic compound selected from the group consisting of ammonia and organic amine so that 20% to 80% by mole, and preferably 30% to 50% by mole of the carboxyl groups in the unit from the monomer (a) is converted into salt form. Further, when the neutralization is performed so that 20% to 80% by mole of the carboxyl groups in the structural unit (a) is converted into free acid group, dispersant having good dispersibility and excellent effect of suppressing pH lowering for calcium carbonate slurry.

If necessary, ammonia and plural organic amines may be used. Basic compounds other than the organic amine may be used in combination therewith as long as the properties of the resulting copolymer are not impaired.

The dispersant can also be obtained by mixing an aqueous solution of the polymer (A) and/or the copolymer (B) with ammonium salt aqueous solution or organic amine salt aqueous solution of (A) and/or (B), and, if necessary, a solution wherein (A) and/or (B) is neutralized with another basic compound in the neutralization ratio as described above.

[0023]

In the present invention, if the ratio of the ammonium salt or organic amine salt in the polymer (A) and/or the copolymer (B) (referred to as (meth)acrylic acid-based (co)polymer in the present invention) exceeds 80%, dispersibility is deteriorated and is therefore unfavorable. It is also industrially unfavorable in terms of odor and cost. On the other hand, if the ratio is less than 20%, the suppressing effect of the pH lowering for calcium carbonate slurry with age is weakened and is therefore unfavorable.

Moreover, if the neutralizing ratio of the acid group in the (meth)acrylic acid-based (co)polymer is less than 20%, pH of the calcium carbonate slurry immediately after grinding is lowered and suppressing effect of the pH lowering for calcium carbonate slurry as mentioned above with age is weakened, being unfavorable.

In addition, the dispersant of the present invention requires that basic compound be used in such a way that the pH of 6.0 or lower is achieved. At the pH of higher than 6.0, the properties of the dispersion liquid slurry such as fluidity, filterability, and the like are insufficient.

[0024]

The basic compound used in the present invention is ammonia or organic amine. The organic amine includes primary amine, secondary amine and tertiary amine.

Examples of the primary amine and secondary amine include aliphatic amine such as lower alkylamine having alkyl group with 1 to 20 carbon atoms including methyl amine, ethyl amine, n-butyl amine, octyl amine, dodecyl amine, dimethyl amine, diethyl amine, dibutyl amine, dioctyl amine, didodecyl amine, and the like as well as alkanolamine such as monoethanol amine, diethanol amine, and the like; (poly)alkylene polyamine such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and the like, derivative of these compounds such as alkylated product, alkylene oxide adduct, and the like; and the like.

The tertiary amine includes tertiary amine and quaternary ammonium salts thereof obtained by quaternization. Examples of the tertiary amine include aliphatic amine such as trimethyl amine, triethyl amine, isopropyl ethyl amine, octyl dimethyl amine, dodecyl dimethyl amine, and the like; alicyclic amine such as N-methyl pyrrolidine, N-ethylpyrrolidine, N-methyl piperidine, N-ethyl piperidine, and the like; aromatic amine such as N,N-dimethyl aniline, N,N-diethyl aniline, and the like, as well as quaternary ammonium salts of these compounds obtained by quaternization using dialkyl carbonate or other quaternizing agents; and the like.

The basic compound is preferably organic amine, because ammonia

has strong pungent odor. More preferably is alkanolamine or lower alkyl amine. Particularly preferred is monoethanolamine because it has less odor and is environmentally friendly.

[0025]

Examples of the other basic compounds capable of neutralizing the acid group in the (meth)acrylic acid copolymer include alkali metal hydroxide, alkaline-earth metal hydroxide, and the like. The alkali metal is preferably lithium, sodium, potassium, or the like. The alkaline-earth metal is preferably calcium, magnesium, barium, or the like. These compounds may be used singly or mixture of two or more types may be used. Among these, sodium hydroxide is particularly preferred.

However, the use of alkali metal hydroxide or alkaline-earth metal hydroxide alone should be avoided because it leads to the pH lowering of the dispersion liquid slurry.

[0026]

The dispersant of the present invention exhibits excellent effects for inorganic pigment, of particularly calcium carbonate. The amount of the dispersant to be used is usually in the range from 0.01% to 10% by mass, preferably from 0.05% to 5% by mass, and particularly from 0.1% to 3% by mass based on the amount of calcium carbonate. The dispersant cannot exhibit satisfactory dispersion effect in an amount of less than 0.01% by mass. On the other hand, it is also unfavorable to use the dispersant in an amount of greater than 10% by mass, because it tends to lead to the viscosity increasing of the dispersion liquid.

The dispersion liquid of calcium carbonate of the present invention preferably has a pH of 8.0 or higher. If the pH is lower than 8.0, unwanted bacteria are more likely to grow in the slurry, causing the release of unpleasant odor and reducing performances thereof. More preferable pH is 9.5 or higher.

[0027]

Examples of the calcium carbonate used in the present invention include precipitated calcium carbonate, colloidal calcium carbonate, ground calcium carbonate, and the like. Ground calcium carbonate is preferred in terms of cost and other reasons. When ground calcium carbonate coarsely ground with about 400 to 40 mesh (having the size of

about 0.04 mm to 0.4 mm) is used, performances of the dispersant for calcium carbonate of the present invention are maximized.

[0028]

The dispersant of the present invention exhibits excellent effects also as dispersant for inorganic particles such as silica particles, ceria particles (cerium oxide particles), alumina particles, and the like, in addition to the above-mentioned dispersant for inorganic pigment.

[0029]

In general, silica dispersion liquid is used for applications related to papermaking, metalworking, fabrics, paints, optical material and chemical mechanical polishing (hereinafter, referred to as "CMP").

[0030]

CMP is a technique employed for smoothing wafer surface and the like in the manufacturing process of semiconductor devices, wherein a polishing pad is adhered to a polishing platen, the surface of the polishing pad is soaked with abrasive agent and the wafer surface to be polished is pressed against the polishing platen. Then, the polishing platen is rotated with pressure applied thereto, so that any bumps on the surface to be polished are removed by mechanical friction between the abrasive and the bumps, thereby flattening the surface.

Products obtained by dispersing silica particles or ceria particles with the use of dispersant are known as abrasive agent for this CMP.

[0031]

When dispersant liquid of silica particles is produced, the dispersion liquid is preferably used in an amount of 0.01 to 2.0 parts by weight as solid content based on 100 parts by weight of the silica particles.

[0032]

The average size of the silica particles can be appropriately set according to the intended use. In the case of using as abrasive for CMP, the average size is preferably in the range from 0.005 to 0.5 μm .

In the case where the average size is 0.005 μm or greater, when the dispersion liquid is used in the CMP process, large polishing rate can be obtained. On the other hand, when the average size is 0.5 μm or

smaller, the precipitation of the particles can be suppressed.

The amount of the silica particles to be charged is preferably in the range from 0.1% to 50% by weight based on the dispersion liquid. In the case where the content is 0.1% or more by weight, when the dispersion liquid is used in the CMP process, large polishing rate can be obtained. On the other hand, when the content is 50% or less by weight, the aggregation of the particles can be suppressed.

[0033]

On the other hand, ceria dispersion liquid is used for applications related to exhaust gas purifying catalysts, gas sensors, optical material, and CMP.

[0034]

When dispersant liquid of ceria particles is produced, the dispersion liquid is preferably used in an amount of 0.01 to 2.0 parts by weight as solid content based on 100 parts by weight of the ceria particles.

[0035]

The average size of the ceria particles can be appropriately set according to the intended use. In the case of using as abrasive for CMP, the average size is preferably in the range from 0.01 to 1.0 μm .

In the case where the average size is 0.01 μm or greater, when the dispersion liquid is used in the CMP process, large polishing rate can be obtained. On the other hand, when the average size is 1.0 μm or smaller, the precipitation of the particles can be suppressed.

The amount of the ceria particles to be charged is preferably in the range from 0.1% to 50% by weight based on the dispersion liquid. In the case where the content is 0.1% or more by weight, when the dispersion liquid is used in the CMP process, large polishing rate can be obtained. On the other hand, when the content is 50% or less by weight, the aggregation of the particles can be suppressed.

[0036]

Alumina dispersion liquid is used for applications related to papermaking, metalworking, fabrics, paints, optical material and ceramic material.

[0037]

When dispersant liquid of alumina particles is produced, the dispersion liquid is preferably used in an amount of 0.01 to 5.0 parts by weight as solid content based on 100 parts by weight of the alumina particles.

[0038]

The average size of the alumina particles can be appropriately set according to the intended use. The average size is preferably in the range from 0.01 to 5.0 μm .

Setting the average size of the alumina particles to 0.01 μm or greater brings an advantage in terms of cost. On the other hand, when ceramics is produced using alumina particles having the average size is 5.0 μm or smaller, ceramics excellent in high toughness can be obtained.

The amount of the alumina particles to be charged is preferably in the range from 40% to 85% by weight based on the dispersion liquid. In the case where the content is 40% or more by weight, when ceramics is produced using alumina particles, ceramics excellent in dimension accuracy can be obtained. On the other hand, in the case where the content is 85% or less by weight, the viscosity of the dispersion liquid may be lowered and the dispersion liquid can be easily handled.

[0039]

Dispersion liquid containing alumina particles prepared using the dispersant of the present invention can be used for various applications. In particular, dispersion liquid for manufacturing ceramics can be favorably used.

For the foregoing application, ceramic raw powders other than alumina can be used in combination therewith.

As ceramic raw powders, inorganic powders can be used. Example thereof includes metallic oxide such as titania, magnesia, zirconia, and the like; metallic carbide such as silicon carbide, and the like; nitride such as aluminum nitride, silicon nitride, and the like; carbonate such as calcium carbonate, barium carbonate, and the like; barium titanate; and the like.

[EXAMPLES]

[0040]

Hereinafter, the present invention is more specifically explained with Examples. The present invention is no way limited to the following Examples.

In the following examples, "%" and "part(s)" mean "% by mass" and "part(s) by mass".

In the following examples, measurements of weight-average molecular weight (Mw) and number-average molecular weight (Mn) for the (meth)acrylic acid-based (co)polymer, and evaluations for dispersion characteristic of calcium carbonate were made in accordance with the method described below.

[0041]

[1] Weight-average molecular weight (Mw) and number-average molecular weight (Mn) of (meth)acrylic acid-based (co)polymer

A 100- μ L sample obtained in Production Examples described below by extracting the (meth)acrylic acid-based (co)polymer from the neutralized solution and adjusting the concentration to 0.4 wt/vol% was injected to columns [three columns supplied from Tosoh Corporation, "TSKgel G3000PWXL - TSKgel G4000PWXL - TSKgel G6000PWXL" (each has the length of 300 mm and the internal size of 7.8 mm) connected in series] at a column temperature of 35°C. An eluent [buffer solution of 0.1M NaCl and 0.1M phosphoric acid (consisting of 7.70 g of 1N phosphate dihydrate, 36.3 g of 2N phosphate dodecahydrate, 8.63 g of NaCl, and 1,476.4 g of deionized water)] was then passed through the columns at a flow rate of 0.8 ml/min and the weight-average molecular weight (Mw) and number-average molecular weight (Mn) of the (meth)acrylic acid-based (co)polymer were measured using gel permeation chromatography (GPC) method of aqueous system wherein components absorbed to the columns were eluted. The weight-average molecular weight (Mw) and number-average molecular weight (Mn) were calculated by the pre-created calibration curves using, as the reference substance, sodium polyacrylates (with a molecular weight of 9,000,000, 5,550,000, 1,140,000, 440,000, 131,200, 70,900 and 2,400, supplied from American Polymer Standards Corp.) of which weight-average molecular weight (Mw), number-average molecular weight (Mn) and peak top molecular weight (Mp) were known.

[0042]

[2] Dispersion characteristic of calcium carbonate

[2-a] Wet grinding of ground calcium carbonate

900 g of coarsely ground ground calcium carbonate "No.A Jutan" (42-mesh residue: 1% or less, and 100-mesh residue: 90% or more) manufactured by Maruo Calcium Co., Ltd. and 2,970 g of alumina beads (average size 1.0 mm; the medium to be ground) were fed to a dispersing machine (which is a sand grinder) manufactured by Igarashi Kikai K.K. Further, the neutralized aqueous solution of (meth)acrylic acid-based (co)polymer prepared by Production Examples described below was fed to the dispersing machine with the solid content of the (meth)acrylic acid-based (co)polymer being 0.75% by mass based on 900 g of the weight of the ground calcium carbonate. Distillated water was added thereto, and ground calcium carbonate slurry with the concentration of ground calcium carbonate being 75% by mass was prepared inside the dispersing machine. Then, wet grinding was carried out for 50 minutes by rotating the stirring blade of the dispersing machine at a rotation speed of 1,000 rpm.

[0043]

[2-b] Fluidity of ground calcium carbonate slurry during wet grinding

The fluidity of the ground calcium carbonate slurry during the wet grinding in the above [2-a] was evaluated in accordance with the following criteria.

1: There was no material adhering to the stirring blade of the dispersing machine from the early to the late stages of grinding. Fluidity was extremely excellent.

2: Little material was adhering to the stirring blade of the dispersing machine from the early to the late stages of grinding. Fluidity was good.

3: A significant amount of material was adhering to the stirring blade of the dispersing machine from the early to the late stages of grinding (particularly at the early stage). Fluidity was inferior (the fluidity at the early stage of grinding was particularly poor).

[0044]

[2-c] Average size of ground calcium carbonate particles in ground calcium carbonate slurry

The ground calcium carbonate slurry obtained by wet grinding in

the above [2-a] was dispersed in a large amount of deionized water to obtain appropriate light scattering intensity. Using the dispersion as a sample, the average size of the ground calcium carbonate particles in the ground calcium carbonate slurry was determined using laser diffraction/scattering particle size distribution analyzer "LA-920" manufactured by HORIBA Ltd.

[0045]

[2-d] Filterability of ground calcium carbonate slurry

The entire amount of the ground calcium carbonate slurry including the alumina beads obtained by wet grinding in the above [2-a] was used as a sample, which was poured evenly into cylindrical filtration device (the diameter of the filtrating part: 25 cm) with filter cloth having 200 ME attached thereto. At a time where 5 minutes has passed since the filtration was started, the amount (unit: g) of the slurry filtered was measured to evaluate filterability in accordance with the following criteria.

1: At least 40% by mass of the sample passed through the filter cloth. Filterability was extremely excellent.

2: At least 30% and less than 40% by mass of the sample passed through the filter cloth. Filterability was excellent.

3: Only less than 30% by mass of the sample passed through the filter cloth. Filterability was inferior.

[0046]

[2-e] Stability of ground calcium carbonate slurry with age

The filtered product that passed through the filter cloth having 200 ME obtained in the above [2-d] was used as a sample. If the sample was found to have a concentration of ground calcium carbonate of more than 75% by mass, it was diluted with distilled water to adjust the concentration of ground calcium carbonate to 75% by mass. The sample was then left standing at a temperature of 25°C and the initial viscosity of the ground calcium carbonate (immediately after the sample was prepared) and that of 7 days after it was allowed to be left standing were measured by BM-type viscometer manufactured by TOKYO KEIKI INC. at a temperature of 25°C, using a rotor #3 or a rotor #4 (the rotor #3 was used when the viscosity of the sample was not more than 1,000 mPa·s and the rotor #4 was

used when the viscosity of the sample was 1,000 to 1,000 mPa·s) at a rotation speed of 60 rpm.

[0047]

[2-f] pH of ground calcium carbonate slurry

The slurry prepared in the above [2-e] having a concentration of ground calcium carbonate of 75% by mass was used as a sample. Its initial pH value (immediately after the sample was prepared) and pH value of 7 days after it was allowed to be left standing were measured using a pH meter "D-12" manufactured by HORIBA Ltd. in a state where the temperature was regulated to 25°C and evaluation was made in accordance with the following criteria.

1: Both of the initial pH value (immediately after the sample was prepared) and the pH value of 7 days after it was allowed to be left standing were 9.5 or greater.

2: Both of the initial pH value (immediately after the sample was prepared) and the pH value of 7 days after it was allowed to be left standing were below 9.5.

[0048]

Production Example 1 (Production of (meth)acrylic acid-based copolymer (B-1))

(1) A four-neck flask was charged with 114.8 g of isopropyl alcohol and 138.0 g of deionized water. The temperature of the content in the flask was increased to 78°C while stirring at revolution speed of 200 rpm. After the temperature inside the flask became constant, 0.87 g of ammonium persulfate and 4.05 g of deionized water were added all at once. And from 1 minute thereafter, a monomer mixture aqueous solution consisting of 232.2 g of acrylic acid, 37.8g of butyl acrylate and 44.6 g of deionized water (314.6 g in total) and polymerization initiator aqueous solution consisting of 7.83 g of ammonium persulfate and 56.5 g of deionized water (64.3 g in total) were each continuously supplied over 6 hours. After the completion of the continuous supply, the mixture was left keeping at a temperature of 78°C for 1.5 hours to mature, followed by being cooled until the inside temperature was lowered to 50°C. 500 mg of the reaction solution was extracted and analyzed by gas chromatography. Unreacted acryl acid and butyl acrylate were not detected.

(2) After that, the pressure inside the flask was controlled at 80 mmHg by means of a pressure control device and a vacuum pump to distill isopropyl alcohol continuously. The same amount of deionized water as lost via azeotrope formed with isopropyl alcohol was added to the flask.
[0049]

(3) Subsequently, the content in the flask ((meth)acrylic acid-based copolymer, referred to as "B-1" hereinafter) was heated at a temperature of 155°C for 45 minutes and weighed. And then, the amount of (meth)acrylic-based copolymer in the heated aqueous solution was measured. Based on the measured amount, deionized water was added to prepare an aqueous solution with a solid concentration (content of B-1) of 45%.

(4) The aqueous solution with a solid concentration (content of B-1) of 45% obtained in (3) above was subjected to the method [1] above for weight average molecular weight (Mw) and number average molecular weight (Mn) of B-1 contained in the aqueous solution. The results of weight average molecular weight (Mw) of 5,200, number average molecular weight (Mn) of 2,300 and molecular weight distribution (Mw/Mn) of 2.26 were obtained.

[0050]

Production Example 2 (Production of (meth)acrylic acid-based copolymer (B-2))

(1) The polymerization operation was performed in the same manner as those in (1) of Production Example 1 except that monomer mixed aqueous solution consisting of 220.3 g of acrylic acid, 49.7g of polypropylene glycol monoacrylate (number of moles of polypropylene oxide added (n) = 3, terminal hydroxyl group ($R^3 = H$)) and 44.6 g of deionized water (314.6 g in total) was used instead of the monomer mixed aqueous solution in (1) of Production Example 1 (B-1). After the completion of the reaction, 500 mg of the reaction solution was extracted and analyzed by gas chromatography. Unreacted acryl acid and polypropylene glycol monoacrylate were not detected.

(2) Subsequently, the same operations described in (2) and (3) for B-1 were performed to prepare an aqueous solution with a solid concentration (content of (meth)acrylic acid-based copolymer) of 45% (the obtained (meth)acrylic acid-based copolymer is referred to as "B-2" hereinafter).

(3) The aqueous solution with a solid concentration (content of B-2) of 45% obtained in (2) above was subjected to the method [1] above for weight average molecular weight (Mw) and number average molecular weight (Mn) of B-2 contained in the aqueous solution. The results of weight average molecular weight (Mw) of 4,800, number average molecular weight (Mn) of 2,300 and molecular weight distribution (Mw/Mn) of 2.05 were obtained.

[0051]

Production Example 3 (Production of (meth)acrylic acid-based copolymer (A-1))

(1) The polymerization operation was performed in the same manner as those in (1) of Production Example 1 except that monomer aqueous solution consisting of 270.0 g of acrylic acid, and 44.6 g of deionized water (314.6 g in total) was used instead of the monomer mixed aqueous solution in (1) of Production Example 1 (B-1). After the completion of the reaction, 500 mg of the reaction solution was extracted and analyzed by gas chromatography. Unreacted acryl acid was not detected.

(2) Subsequently, the same operations described in (2) and (3) for Production Example 1 were performed to prepare an aqueous solution with a solid concentration (content of (meth)acrylic acid-based copolymer) of 45% (the obtained (meth)acrylic acid-based copolymer is referred to as "A-1" hereinafter).

(3) The aqueous solution with a solid concentration (content of A-1) of 45% obtained in (2) above was subjected to the method [1] above for weight average molecular weight (Mw) and number average molecular weight (Mn) of A-1 contained in the aqueous solution. The results of weight average molecular weight (Mw) of 5,300, number average molecular weight (Mn) of 2,400 and molecular weight distribution (Mw/Mn) of 2.21 were obtained.

[0052]

Dispersants were prepared by using the (meth)acrylic acid-based (co)polymers (B-1), (B-2) and (A-1) each obtained in Production Examples 1 to 3, and neutralizing some or all of the acid groups in (B-1), (B-2) and (A-1) in accordance with the neutralization method described in each of Examples below. Wet grinding of the ground calcium carbonate was

carried out by the method described in [2-a] above. Then, the fluidity of the ground calcium carbonate slurry during wet grinding was evaluated in accordance with the method described in [2-b] above.

Further, the average size of the ground calcium carbonate particles contained in the ground calcium carbonate slurry obtained by wet grinding was measured by the method described in [2-c] above to evaluate the filterability of the slurry by the method described in [2-d] above. Moreover, the stability of the slurry with age was evaluated by the method described in [2-e] above and lastly, the pH value of the slurry was evaluated by the method described in [2-f] above.

In the following, the evaluation results of Examples are shown in Table 1 and those of Comparative Examples are shown in Table 2.

[0053]

Example 1

The aqueous solution of (meth)acrylic acid-based copolymer B-1 was used. The flask was cooled with iced water. While measuring the pH, 48% sodium hydroxide aqueous solution was supplied to neutralize 20% of the carboxyl groups derived from acrylic acid and further, monoethanolamine was supplied to neutralize 30% of the carboxyl groups derived from acrylic acid. Neutralized copolymer having a solid content of 42.0% and pH of 5.0 was prepared.

The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The viscosity of the dispersion liquid slurry was measured as 610 mPa·s on the day of wet grinding and as 930 mPa·s seven days thereafter. The median size of the dispersion liquid immediately after production was measured as 0.604 μm and the content ratio of the particles of 1.32 μm or less was found to be 98%. The pH of the dispersion liquid slurry was measured to be 9.8 on the day of wet grinding and 9.8 seven days thereafter.

[0054]

Example 2

Neutralization was conducted in the same manner as that in Example 1 except using the (meth)acrylic acid-based copolymer B-2 instead of the (meth)acrylic acid-based copolymer B-1 used in Example 1. Accordingly,

dispersant for pigment having a solid content of 41.2% and pH of 5.1 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0055]

Example 3

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 20% with monoethanolamine and 30% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 42.1% and pH of 5.0 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0056]

Example 4

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be only 30% with monoethanolamine. Accordingly, dispersant for pigment having a solid content of 42.9% and pH of 4.4 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0057]

Example 5

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 30% with monoethanolamine and 50% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 41.2% and pH of 5.9 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0058]

Example 6

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be only 50% with monoethanolamine. Accordingly, dispersant for pigment having a solid content of 43.0% and pH of 5.2 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0059]

Example 7

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be only 80% with monoethanolamine. Accordingly, dispersant for pigment having a solid content of 43.4% and pH of 5.9 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0060]

Example 8

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be only 50% with ammonia. Accordingly, dispersant for pigment having a solid content of 40% and pH of 4.9 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0061]

Example 9

Neutralization was conducted in the same manner as that in Example 1 except using the (meth)acrylic acid-based copolymer A-1 instead of the (meth)acrylic acid-based copolymer B-1 used in Example 1. Accordingly, dispersant for pigment having a solid content of 42.3% and pH of 5.1 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was

evaluated.

[0062]

Comparative Example 1

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 97% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 40% and pH of 8.0 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0063]

Comparative Example 2

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 30% with monoethanolamine and 67% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 40.7% and pH of 8.1 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0064]

Comparative Example 3

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 50% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 40.5% and pH of 5.1 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0065]

Comparative Example 4

Neutralization was conducted in the same manner as that in Example 1 except that the neutralization rate was set to be 97.0% with monoethanolamine. Accordingly, dispersant for pigment having a solid content of 43.2% and pH of 8.2 was obtained. The ground calcium carbonate

was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0066]

Comparative Example 5

Neutralization was conducted in the same manner as that in Example 1 except that the (meth)acrylic acid-based copolymer A-1 was used instead of the (meth)acrylic acid-based copolymer B-1 used in Example 1 and that the neutralization rate was set to be 30% with monoethanolamine and 67% with 48% sodium hydroxide aqueous solution. Accordingly, dispersant for pigment having a solid content of 39.9% and pH of 8.0 was obtained. The ground calcium carbonate was subjected to wet grinding using this neutralized copolymer according to the method described in [2-a]. The dispersion characteristic of the dispersion liquid slurry was evaluated.

[0067]

Table 1

		Elapsed days (60rpm)		Median size (μm)	Slurry NV (%)	Slurry pH	Slurry fluidity	Slurry filterability
		Immediately after grinding	After 1 week					
Example 1	B-1	610	930	0.604	75.0	1	1	1
Example 2	B-2	700	930	0.603	75.0	1	1	1
Example 3	B-1	510	850	0.588	75.0	1	1	1
Example 4	B-1	720	990	0.630	75.0	1	1	1
Example 5	B-1	730	2700	0.589	75.1	1	2	1
Example 6	B-1	820	1640	0.618	75.1	1	1	1
Example 7	B-1	700	2700	0.599	75.1	1	2	1
Example 8	B-1	560	1350	0.598	75.0	1	1	1
Example 9	A-1	970	1340	0.635	75.2	1	1	2

Table 2

		Elapsed days (60rpm)		Median size (μm)	Slurry NV (%)	Slurry pH	Slurry fluidity	Slurry filterability
		Immediately after grinding	After 1 week					
Comparative Example 1	B-1	750	4850	0.567	75.1	1	3	2
Comparative Example 2	B-1	970	4800	0.592	75.2	1	3	2
Comparative Example 3	B-1	680	1400	0.581	75.2	2	1	1
Comparative Example 4	B-1	1600	4630	0.588	75.2	1	3	2
Comparative Example 5	A-1	940	5050	0.552	75.1	1	3	3

[INDUSTRIAL APPLICABILITY]

[0069]

The present invention provides dispersant for inorganic pigment, particularly dispersant for calcium carbonate which is used for high concentrated pigment slurry with solid or dispersant slurry having extremely small particle sizes.

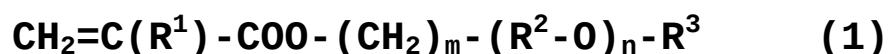
When the dispersant of the present invention is used, excellent effect of stabilizing dispersing pigment is obtained and the dispersant makes it possible to disperse them in fine particles while maintaining good fluidity. Therefore, dispersion liquid can be prepared which is stable in viscosity increase and pH of the slurry with age for a long time. The dispersion liquid is very suitable for use in the papermaking industry as well as for applications in plastics, rubbers, paints, inks, adhesives, sealants and the like.

What is claimed is:

1. A dispersant for calcium carbonate having pH of 6.0 or lower, characterized in that said dispersant is partially neutralized product of (A) polymer of (a) α,β -unsaturated carboxylic acid or (B) copolymer consisting of 80% to 99% by mole of a unit derived from (a) α,β -unsaturated carboxylic acid and 1% to 20% by mole of at least one unit selected from the group consisting of a unit derived from (b) (meth)acrylic acid ester and a unit derived from (c) (meth)acrylic acid ester of polyalkylene glycol, based on 100% by mole of the total of (a), (b) and (c), that 20% to 80% by mole of the acid group is partially neutralized with ammonia or organic amine, and that said polymer (A) or said polymer (B) is neutralized so that 20% to 80% by mole of the carboxyl groups derived from said α,β -unsaturated carboxylic acid (a) is converted into free acid group.

2. The dispersant for calcium carbonate according to Claim 1, wherein 20% to 50% by mole of the acid group in said polymer (A) or said copolymer (B) is partially neutralized with ammonia or organic amine, and wherein said polymer (A) or said copolymer (B) is neutralized so that 50% to 70% by mole of the carboxyl groups derived from said α,β -unsaturated carboxylic acid (a) is converted into free acid group.

3. The dispersant for calcium carbonate according to Claim 1 or 2, wherein said monomer (b) for forming said copolymer (B) is (meth)acrylic acid ester with 1 to 8 carbon atoms, and said monomer (c) is (meth)acrylic acid ester of polyalkylene glycol represented by the following general formula (1):



wherein R^1 is hydrogen atom or methyl group, R^2 is ethylene group or propylene group, R^3 is hydrogen atom or alkyl group with 1 to 6 carbon atoms, m is the number of 0 to 4, and n is the number of 2 to 10.

4. The dispersant for calcium carbonate according to any one of Claims 1 to 3, wherein said acid group in said unit derived from said monomer (a) in said polymer (A) or said copolymer (B) is in a form of organic

amine salt.

5. The dispersant for calcium carbonate according to any one of Claims 1 to 4, wherein the weight average molecular weight (Mw) of said polymer (A) or said copolymer (B) is in the range from 4,000 to 8,000 based on polyacrylic acid standard by gel permeation chromatography, and Mw/Mn (weight average molecular weight/number average molecular weight) is 2.7 or less.

6. The dispersant for calcium carbonate according to any one of Claims 1 to 5, wherein said dispersant is of said copolymer (B).

7. The dispersant for calcium carbonate according to any one of Claims 1 to 6, wherein said monomer (a) for forming said copolymer (B) is acrylic acid, said monomer (b) is butyl acrylate, and said monomer (c) is polypropylene glycol mono (meth)acrylate where R² in said general formula (1) is propylene group.

8. The dispersant for calcium carbonate according to any one of Claims 1 to 7, wherein said organic amine is monoethanol amine.

9. A dispersion of calcium carbonate having pH of 9.5 or higher, which is prepared by wet grinding using said dispersant for calcium carbonate according to any one of Claims 1 to 8 by wet grinding.

10. The dispersion of calcium carbonate according to Claim 9, wherein said calcium carbonate is ground calcium carbonate.