

## SPECIFICATION

### PIGMENT DISPERSANT

#### [TECHNICAL FIELD]

[0001]

The present invention relates to a pigment dispersant for a pigment of calcium carbonate or the like. More specifically, the present invention provides a pigment dispersant of a (meth)acrylic acid based copolymer, being capable of dispersing an inorganic pigment while maintaining higher dispersion stabilizing effect and good fluidity in the state of fine particles, particularly when used as a dispersant for the inorganic pigment of small particle size, as well as capable of stably dispersing an inorganic pigment in a solution such as water for an extended period while the increasing viscosity is suppressed over time.

In the present invention, (meth)acrylic acid or part or whole thereof that has been neutralized is referred to as (meth)acrylic acid (salt).

#### [BACKGROUND ART]

[0002]

Conventionally, a homopolymer of acrylic acid (salt) and a copolymer of acrylic acid (salt) and other copolymerizable monomer have been known as a dispersant for an inorganic pigment. When a homopolymer and a copolymer of acrylic acid (salt) adsorb on pigment particles, the polymer imparts the repulsion action between particles due to the steric hindrance to form a stable pigment dispersion liquid. In particular, an acrylic acid (salt) copolymer has an advantage over an acrylic acid (salt) homopolymer, and the following proposals have been made.

According to Patent Document 1 (JP-A S61-69872), wet grinding of calcium carbonate is performed using a dispersant consisting of a copolymer formed from a monomer including a monocarboxylic acid (salt),

a monomer including a dicarboxylic acid (salt) and a (meth) acrylic ester monomer.

According to Patent Document 2 (JP-A S56-115630), a dispersing of a pigment is performed using a dispersant consisting of a copolymer formed from a monomer including a carboxylic acid (salt), a (meth)acrylic ester monomer with 1 to 8 carbon atoms and a monomer including a sulfonic acid (salt).

[0003]

According to Patent Document 3 (JP-A S49-130915), a dispersing of a pigment is performed using a dispersant consisting of a copolymer formed from a monomer including a carboxylic acid (salt) and a (meth)acrylic ester monomer with 1 to 4 carbon atoms.

According to Patent Document 4 (JP-A 2004-306022), a dispersing of a precipitated calcium carbonate is performed using a dispersant consisting of a copolymer formed from a monomer including a carboxylic acid (salt) and a (meth)acrylic ester monomer with 1 to 20 carbon atoms in a ratio of 97-99:1-3.

Further, according to Patent Document 5 (JP-A S55-18423), a dispersing of a pigment is performed using a dispersant consisting of a copolymer formed from a (meth)acrylic acid (salt) and a (meth)acrylic ester monomer with 1 to 12 carbon atoms.

[0004]

However, in recent years, an inorganic pigment having smaller particle size compared with the conventional pigments has become used, and a dispersant has been required to reduce exothermic heat generated when the wet grinding is carried out, to as little as possible. In addition, improvements in separation between dispersion media and slurry have become required.

An inorganic pigment having small particle size tends to increase the viscosity of the dispersion liquid because the interaction between particles becomes stronger due to the increased surface area and thus such particles become easy to be cohered each other. Moreover, exothermic heat becomes larger due to intensive repeated collisions of the particles during wet grinding. Furthermore,

separation of dispersion media and slurry tends to worsen if the particle size is small, and the amount of the slurry to be collected becomes smaller.

[0005]

For such demands, satisfactory performances have not been obtained by the above-mentioned dispersants.

For example, in the dispersant described in Patent Document 1 (JP-A S61-69872), Patent Document 2 (JP-A S56-115630), Patent Document 3 (JP-A S49-130915), Patent Document 4 (JP-A 2004-306022), there are problems that the viscosity of the dispersion liquid becomes higher over time and the exothermic heat becomes larger when the wet grinding is carried out. Furthermore, there is also a problem that the amount of the slurry to be collected becomes smaller.

Moreover, the emulsifying agent used according to Patent Document 5 (JP-A S55-18423) affects the dispersibility adversely, and there are problems like as in the Patent Document 1, that the viscosity of the dispersion liquid becomes higher and the exothermic heat becomes larger when the wet grinding is carried out. In addition, there is also a problem that the amount of the slurry to be collected becomes smaller.

Thus, even if a copolymer of acrylic acid (salt) mentioned above is used, a dispersant which is satisfactory with respect to dispersion stabilizing effect of an inorganic pigment having small particle size, suppression of exothermic heat during wet grinding, and the amount of slurry to be collected has not been obtained.

[0006]

Patent Document 1: JP-A S61-69872

Patent Document 2: JP-A S56-115630

Patent Document 3: JP-A S49-130915

Patent Document 4: JP-A 2004-306022

Patent Document 5: JP-A S55-18423

[DISCLOSURE OF THE INVENTION]

[PROBLEMS THAT THE INVENTION IS TO SOLVE]

[0007]

The object of the present invention is to provide a (meth)acrylic acid based pigment dispersant that satisfies an improved dispersibility of an inorganic pigment having small particle size and a suppressing effect on exothermic heat during wet grinding, which has been required for a recent dispersant.

[MEANS FOR SOLVING THE PROBLEMS]

[0008]

The present inventors selected a specific (meth)acrylic acid alkyl ester having carbon atoms of 4 to 8 as a (meth)acrylic acid alkyl ester for the conventionally known copolymer of a (meth)acrylic acid and (meth)acrylic acid alkyl ester in order to solve the above problems. As a result, it is found that a dispersant consisting of an obtained (meth)acrylic acid based copolymer and an alcohol having carbon atoms of 4 to 8, in other words, a pigment dispersant in which weight ratio of the alcohol having carbon atoms of 4 to 8 is in the range from 1,000 ppm to 30,000 ppm based on the (meth)acrylic acid based copolymer could solve the above problems. And the present invention was completed.

[0009]

The present invention for solving the above-mentioned problems is as follows.

The first invention is a pigment dispersant which contains a (meth)acrylic acid based copolymer obtained using as essential components a (meth)acrylic acid monomer and a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8, and an alcohol having carbon atoms of 4 to 8, and is a pigment dispersant in which the weight ratio of the alcohol having carbon atoms of 4 to 8 is in the range from 1,000 ppm to 30,000 ppm based on the (meth)acrylic acid based copolymer.

The second invention is a pigment dispersant according to the first invention, wherein weight ratio of said alcohol having carbon atoms of 4 to 8 is in the range from 2,000 ppm to 15,000 ppm based on

the (meth)acrylic acid based copolymer.

The third invention is a pigment dispersant according to the first or second invention, wherein the (meth)acrylic acid based copolymer is obtained using 60% to 95% by weight of the (meth)acrylic acid monomer, 5% to 40% by weight of a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8, and 0% to 10% by weight of other monomer capable of copolymerizing with the (meth)acrylic acid monomer and the (meth)acrylic acid alkyl ester monomer.

The fourth invention is a pigment dispersant according to any one of the first to third inventions, wherein the (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8 is a butyl (meth)acrylate, and the alcohol having carbon atoms of 4 to 8 is a butyl alcohol.

The fifth invention is a pigment dispersant according to any one of the first to fourth inventions, wherein the pigment dispersant is a dispersant for wet grinding.

The sixth invention is a wet grinding method of a pigment characterized in that the pigment dispersant according to any one of the first to fourth inventions is used for the wet grinding of the pigment.

#### [EFFECT OF THE INVENTION]

[0010]

According to the pigment dispersant containing a (meth)acrylic acid (salt) based copolymer of the present invention, when it is used as a dispersant for an inorganic pigment having a small particle size, the viscosity of the dispersion liquid is not increased over time, the exothermic heat during wet grinding can be suppressed, and the amount of the slurry to be collected is large. Therefore, the dispersant is useful as a dispersant in various uses.

It is estimated that the appearance of the effect as the pigment dispersant in the present invention is based on the adsorption of the dispersant of the present invention on the particles in the

dispersion liquid as well as simultaneous impartment of smoothness between particles and between slurry and dispersion media, as compared with a conventional dispersant.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0011]

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

The pigment dispersant of the present invention is characterized by being containing a (meth)acrylic acid based copolymer obtained using as essential components a (meth)acrylic acid monomer and a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8, and an alcohol having carbon atoms of 4 to 8, and is further characterized in that the weight ratio of the alcohol having carbon atoms of 4 to 8 is in the range from 1,000 ppm to 30,000 ppm based on the (meth)acrylic acid based copolymer.

[0012]

The (meth)acrylic acid includes acrylic acid and methacrylic acid, and it may be a partly or fully neutralized salt form thereof that is a (meth)acrylic acid salt. Among them, acrylic acid and/or acrylic acid salt is preferable from a viewpoint of polymerizability in the production of a copolymer and water-solubility.

Examples of the (meth)acrylic acid salt include an alkali metal salt such as sodium salt, potassium salt or lithium salt, of (meth)acrylic acid; an ammonium salt of (meth)acrylic acid; an organic amine salt such as diethanolamine salt or triethanolamine salt, of (meth)acrylic acid; and the like. From a viewpoint of the balance between production cost and performance, the (meth)acrylic acid salt is preferably in the form of an alkali metal salt, and particularly in the form of a sodium salt.

The (meth)acrylic acid salt can be produced by reacting (meth)acrylic acid with an alkali metal hydroxide such as sodium hydroxide and potassium hydroxide, ammonia, or an organic amine such as monoethanol amine.

[0013]

In the (meth)acrylic acid based copolymer according to the present invention, all the carboxyl groups in the (meth)acrylic acid may be unneutralized carboxyl groups. But the carboxyl groups are neutralized in an amount of preferably 15% to 100% by mol, and particularly 25% to 100% by mol with a base and it is preferable that the copolymer is in the form of a salt since the water-solubility of the (meth)acrylic acid based copolymer is improved and the dispersion stabilizing effect becomes higher.

In addition, with respect to the pH, it is desirable that the carboxyl groups are neutralized with a base in such a ratio that the pH of the aqueous solution of the (meth)acrylic acid based copolymer is in the range from 3 to 9, and particularly from 4 to 8 since the water-solubility of the (meth)acrylic acid based copolymer is improved and the dispersion stabilizing effect becomes higher.

[0014]

Before and during the step of polymerization for producing the (meth)acrylic acid based copolymer, it is preferable, from a viewpoint of progress of smooth polymerization reaction, that polymerization is carried out in such a manner that at least 40% by mol (40% to 100% by mol) of the carboxyl groups in the (meth)acrylic acid are unneutralized, and after the polymerization preferably 15% or more by mol, and more preferably 25% or more by mol of the carboxyl groups in the (meth)acrylic acid based copolymer are converted into a salt form with a basic compound.

[0015]

Examples of the (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8 include n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, and the like. Among these, butyl (meth)acrylate including n-butyl (meth)acrylate, isobutyl (meth)acrylate and t-butyl (meth)acrylate are preferable. And particularly preferred is n-butyl (meth)acrylate.

If a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 3 or smaller is used, the viscosity of the dispersion liquid tends to be increased and the dispersion liquid tends to increase the exothermic heat at the time of wet grinding, which is unfavorable. Additionally, the amount of the slurry to be collected becomes small, which is unfavorable. It is estimated that this is because sliding impartment to particles is small. On the other hand, if a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 9 or more is used, the dispersion liquid tends to be separated, which is not desirable.

[0016]

The weight ratio of the (meth)acrylic acid (salt) to the (meth)acrylic acid alkyl ester with an alkyl group having 4 to 8 carbon atoms is preferably from 95:5 to 60:40 and more preferably from 90:10 to 70:30 of (meth)acrylic acid (salt) and (meth)acrylic acid alkyl ester.

If the (meth)acrylic acid (salt) is less than 60% by weight, the pigment dispersant may be separated. On the other hand, if the (meth)acrylic acid (salt) exceeds 95% by weight, the viscosity of the dispersion liquid tends to be increased, which is not favorable.

[0017]

In the (meth)acrylic acid based copolymer according to the present invention, a monomer which is copolymerizable with the (meth)acrylic acid (salt) and the (meth)acrylic acid alkyl ester may be copolymerized in addition to the (meth)acrylic acid (salt) and the (meth)acrylic acid alkyl ester. Example thereof include an unsaturated acid such as maleic acid and itaconic acid, and a salt thereof, an unsaturated anhydride such as maleic anhydride and itaconic anhydride, an unsaturated sulfonic acid such as 2-acrylamide-2-methylpropanesulfonic acid and styrene sulfonic acid, and a salt thereof, a hydroxyalkyl ester of a (meth)acrylic acid, acrylamide, a (meth)acrylic acid ester having a polyalkyleneoxide structure in the ester part, and the like. The monomer may be used singly or in combination of two or more types thereof.

The amount of the other monomer to be used in the range from 0 to 10 parts by weight, and more preferably from 0 to 5 parts by weight based on 100 parts by weight of the total of the monomer. If the amount exceeds 10 parts by weight, the viscosity of the dispersion liquid tends to be increased, which is unfavorable.

[0018]

The production method of the (meth)acrylic acid based copolymer is not particularly limited. The (meth)acrylic acid based copolymer can be produced by solution polymerization, aqueous solution polymerization, high temperature and high pressure polymerization, inverse suspension polymerization, emulsion polymerization, and the like. Among these, solution polymerization and aqueous solution polymerization are preferable and aqueous solution polymerization is particularly preferred.

According to the aqueous polymerization, a dispersant can be obtained as a homogenous solution. On the other hand, when the dispersant is produced by other polymerization methods such as emulsion polymerization, a homogeneous solution cannot be obtained. Accordingly, only a heterogeneous dispersing can be performed and the viscosity of the resultant dispersion liquid tends to be increased, which is not desirable.

As a solvent for the aqueous polymerization, it is preferable to use a mixture of water and an organic solvent. If only water is used, the (meth)acrylic acid alkyl ester is hard to be dissolved, which is unfavorable. On the other hand, if only an organic solvent is used, it is necessary to substitute the organic solvent by water in the case of using the product as the dispersant and it takes cost and effort, which is not desirable.

Preferable example of the organic solvent includes an alcohol such as isopropyl alcohol, and a ketone such as acetone. Particularly preferred is isopropyl alcohol.

[0019]

In addition, the polymerization initiator for the polymerization reaction is not particularly limited and conventionally

known polymerization initiator can be used. Particularly preferred is a radical polymerization initiator.

Examples of the radical polymerization initiator include a water-soluble peroxide such as a peroxosulfate including sodium peroxodisulfate, potassium peroxodisulfate and ammonium peroxodisulfate; a hydroperoxide such as t-butyl hydroperoxide; and hydrogen peroxide; an oil-soluble peroxide such as a ketone peroxide including methylethylketone peroxide and cyclohexanone peroxide; a dialkyl peroxide including di-t-butyl peroxide and t-butylcumyl peroxide.

The above-mentioned peroxide based radical polymerization initiator may be used singly or in combination of two or more types thereof.

Among the above-mentioned peroxide based radical polymerization initiator, it is preferred to use hydrogen peroxide and a peroxide such as a persulfate salt which are easy to regulate the molecular weight and have a low decomposition point. Particularly preferred is a persulfate salt such as sodium persulfate and ammonium persulfate.

[0020]

The amount of the radical polymerization initiator to be used is preferably in the range from 0.1% to 15% by weight and particularly from 0.5% to 10% by weight based on the total weight of the whole monomers for the (meth)acrylic acid based copolymer. If the amount of the radical polymerization initiator to be used is less than 0.1% by weight, copolymerization rate is decreased. On the other hand, if the amount of the radical polymerization initiator to be used exceeds 15% by weight, the stability of the (meth)acrylic acid based copolymer may be lowered and performances as the dispersant may be affected adversely by the copolymer.

[0021]

In some cases, the (meth)acrylic acid based copolymer may be produced using a water-soluble redox-based polymerization initiator. The redox-based polymerization initiator may be one which an oxidizing agent such as the above-mentioned peroxide and a reducing agent such

as sodium hydrogen sulfite, sodium sulfite and sodium hydrosulfite, iron alum, potassium alum, or the like are combined.

[0022]

In the production of the (meth)acrylic acid based copolymer, a chain transfer agent may be added to the polymerization system in an appropriate amount so as to adjust the molecular weight. Examples of the usable chain transfer agent include sodium phosphite, sodium hypophosphite, sodium bisulfite, mercaptoacetic acid, mercaptopropionic acid, 2-propanethiol, 2-mercaptoethanol, thiophenol, and the like.

[0023]

The polymerization temperature for the production of the (meth)acrylic acid based copolymer is not particularly limited. It is possible to perform the polymerization at a wide range of temperatures, but the polymerization temperature is preferably in the range from 60°C to 100°C.

If the polymerization temperature is lower than 60°C, it is unfavorable in terms of productivity because the polymerization reaction becomes slow. In addition, the reaction may be carried out under pressure or reduced pressure, but cost is required for facilities for use under pressure or reduced pressure. Thus, the polymerization is preferably performed under normal pressure.

The polymerization time is preferably in the range from 2 to 20 hours, and particularly from 3 to 10 hours.

[0024]

The weight average molecular weight of the (meth)acrylic acid based copolymer is preferably in the range from 2,000 to 10,000, and more preferably from 3,000 to 8,000. If the weight average molecular weight is less than 2,000, the viscosity of the dispersion liquid tends to be increased due to easy desorption of the dispersant from the particles in the dispersion liquid, which is not desirable. On the other hand, if the weight average molecular weight exceeds 10,000, the dispersant itself increases the viscosity of the dispersion liquid and thus tends to increase the viscosity of the dispersion liquid,

which is not desirable. It is noted that the weight average molecular weight is an estimated value with GPC (gel permeation chromatography).  
[0025]

After an organic solvent is removed from a solution containing the (meth)acrylic acid based copolymer through distillation, vacuum distillation or drying, the obtained (meth)acrylic acid based copolymer is made water-soluble by optionally converting the carboxyl group of the (meth)acrylic acid into a salt form by neutralization with a basic compound. The neutralization is, as mentioned above, carried out in such a manner that preferably 15% to 100% by mol and particularly 25% to 100% by mol of the carboxyl groups are neutralized with a base to form a salt.

Examples of the basic compound for the neutralization include a hydroxide of an alkali metal such as sodium hydroxide and potassium hydroxide, ammonia water, an organic amine such as diethanol amine and triethanol amine, and the like. Among these, sodium hydroxide and/or potassium hydroxide are preferable, and sodium hydroxide is particularly preferred.

[0026]

The obtained water-solubilized (meth)acrylic acid based copolymer is used as a dispersant by addition of an alcohol with 4 to 8 carbon atoms. The content of the alcohol with 4 to 8 carbon atoms is in the range from 1,000 ppm to 30,000 ppm, preferably from 1,500 ppm to 20,000 ppm, and particularly from 2,000 to 15,000 ppm with respect to the (meth)acrylic acid based copolymer.

If the content of the alcohol is less than 1,000 ppm, the viscosity of the dispersion liquid tends to be increased due to small impartment of smoothness between the particles, and tends to increase exothermic heat during wet grinding, which is not desirable. In addition, this case is not desirable because the amount of slurry to be collected becomes less. On the other hand, if the content of the alcohol exceeds 30,000 ppm, the aggregation of the particles easily occurs and the viscosity of the dispersion liquid tends to be higher, which is not desirable.

[0027]

Examples of the alcohol having 4 to 8 carbon atoms include n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, pentyl alcohol, n-hexyl alcohol, heptyl alcohol, octyl alcohol and 2-ethylhexyl alcohol. Among these, n-butyl alcohol, isobutyl alcohol and t-butyl alcohol are preferable from the viewpoint of performances as the dispersant. Particularly preferred is a n-butyl alcohol.

If the alcohol is one having carbon atoms of 3 or less, the viscosity of the dispersion liquid may be higher and the dispersion liquid has a tendency to increase exothermic heat on wet grinding, which is not desirable. In addition, this case is not desirable because the amount of slurry to be collected may be decreased, being unfavorable. On the other hand, the alcohol is one having 9 or more carbon atoms, the dispersant tends to be separated, which is not desirable.

[0028]

The pigment dispersant of the present invention is usually prepared so as to make solid content concentration in the range from 50% to 80% by weight. The concentration is preferably from 60% to 78% by weight. It is preferable to add water to adjust the concentration.

[0029]

The pigment dispersant of the present invention exhibits an excellent effect for an inorganic pigment. Specific examples include clay, ground calcium carbonate, precipitated calcium carbonate, titanium oxide, alumina, satin white, and the like.

The pigment dispersant of the present invention is usually used in an amount from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight, and particularly from 0.1% to 3% by weight relative to the pigment. If the amount of the pigment dispersant to be used is less than 0.01% by weight, dispersing effect is insufficient. On the other hand, if the amount of the pigment dispersant to be used is more than 10% by weight, the viscosity of the slurry or the like tends to be higher, which is not unfavorable.

[EXAMPLES]

[0030]

Hereinafter, the present invention is described in detail using Examples. In the following description, "%" means % by weight and "part" means part by weight unless otherwise indicated.

#### Example 1

Into a tank reactor equipped with a stirrer and a condenser were fed 170 kg of deionized water and 250 kg of isopropyl alcohol, and the mixture was kept at a temperature of 80°C. A monomer (330 kg) consisting of a mixture of 255 kg of acrylic acid and 75 kg of n-butyl acrylate, and 60 kg of 15% ammonium persulfate aqueous solution were supplied to this reactor over a period of 5 hours. After completion of the addition by dropping, the reaction solution was kept at 80°C for one hour. Subsequently, isopropyl alcohol was removed by evaporation under reduced pressure while adding deionized water. After that, the reaction solution was kept at 50°C and 48% sodium hydroxide aqueous solution was added over a period of 4 hours to neutralize. Here, when the neutralized reaction solution was analyzed with gas chromatography, 300 ppm of n-butanol was detected. Thus n-butanol was further added to adjust to 1,500 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 1,500 ppm of n-butanol was obtained.

The weight-average molecular weight (Mw) of the resultant pigment dispersant was measured by gel permeation chromatography (GPC). GPC was performed with "HLC 8020 system" manufactured by Tosoh Corp. As the column, "G4000PW<sub>XL</sub>", "G3000PW<sub>XL</sub>" and "G2500PW<sub>XL</sub>" manufactured by Tosoh Corp. were connected sequentially to use. As an eluent, 0.1M-NaCl and phosphate buffer (pH7) were used in combination. A calibration curve was prepared using sodium polyacrylate manufactured by Sowa Kagaku Ltd. As a result of measurement, the Mw was found to be 6,000.

[0031]

Into a cylindrical container charged with 17 g of the pigment

dispersant obtained above, 320 g of deionized water, and 900 g of ground calcium carbonate ("Tankaru A" manufactured by Maruo Calcium Co., Ltd.). They were stirred lightly for homogeneous mixing. Subsequently, 3,000 g of dispersion media (sand) was added and wet grinding was carried out by stirring at 1,000 rpm for 50 minutes. When the temperature of the solution after completion of the stirring was measured with a thermometer, it was found to be 79°C. After that, the dispersion liquid was collected through a filter cloth having 200 ME. When the amount of the dispersion liquid collected was measured, it was found to be 390 g. Ion exchanged water was added to this slurry so that the solid content concentration was adjusted to 75%, thereby to give a dispersion liquid.

The fluidity of the ground calcium carbonate slurry during the wet grinding was evaluated according to the following criteria.

A: The separation of the slurry and the dispersion media after the grinding was extremely prompt, and the fluidity of the slurry was extremely excellent.

B: The separation of the slurry and the dispersion media after the grinding was prompt, and the fluidity of the slurry was excellent.

C: The separation of the slurry and the dispersion media after the grinding did not proceed promptly, and the fluidity of the slurry was low.

[0032]

The viscosity of the slurry of the dispersion liquid on that day of the wet grinding and the viscosity of the slurry of the dispersion liquid after being allowed to stand at 25°C for 7 days were measured using a BL viscometer under the conditions of 25°C and 60 rpm. The viscosity of the slurry on the wet grinding day was found to be 250 mPa·s, and the viscosity of the slurry on day 7 after being allowed to stand was found to be 2,200 mPa·s.

In addition, the median diameter and the integrated value under 1.32  $\mu\text{m}$  of the dispersion liquid immediately after the production were measured using a laser diffraction/scattering particle size distribution analyzer ("LA-910" manufactured by Horiba, Ltd.). The

median diameter was 0.67  $\mu\text{m}$  and the value under 1.32  $\mu\text{m}$  was 100%.

These results were shown in Table 1.

[0033]

#### Example 2

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 290 kg of acrylic acid and 40 kg of 2-ethylhexyl acrylate were used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 100 ppm of 2-ethylhexanol was detected. Thus 2-ethylhexanol was further added to adjust to 3,000 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 3,000 ppm of 2-ethylhexanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0034]

#### Example 3

Polymerization and evaporation under reduced pressure were carried out in a similar manner to Example 1, except that 230 kg of acrylic acid and 100 kg of n-butyl acrylate were used instead of the monomer used in Example 1. After that, the reaction solution was kept at a temperature of 80°C, and 48% sodium hydroxide aqueous solution was added over a period of 4 hours to neutralize. When the neutralized reaction solution was analyzed, 800 ppm of n-butanol was detected. Additional alcohol was not added any more. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 800 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0035]

#### Example 4

Polymerization and evaporation under reduced pressure were carried out in a similar manner to Example 1, except that 270 kg of acrylic acid and 60 kg of n-butyl acrylate were used instead of the monomer used in Example 1. After that, the reaction solution was kept at a temperature of 70°C, and 48% sodium hydroxide aqueous solution

was added over a period of 4 hours to neutralize. When the neutralized reaction solution was analyzed, 500 ppm of n-butanol was detected. N-butanol was further added to adjust to 5,000 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 7, and 5,000 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0036]

#### Example 5

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 290 kg of acrylic acid and 40 kg of isobutyl acrylate were used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 100 ppm of isobutanol was detected. Thus isobutanol was further added to adjust to 2,000 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 2,000 ppm of isobutanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0037]

#### Example 6

Polymerization and evaporation under reduced pressure were carried out in a similar manner to Example 1, except that 255 kg of acrylic acid and 75 kg of n-butyl acrylate were used instead of the monomer used in Example 1. After that, the reaction solution was kept at a temperature of 60°C, and 48% sodium hydroxide aqueous solution was added over a period of 4 hours to neutralize. When the neutralized reaction solution was analyzed, 400 ppm of n-butanol was detected. Thus n-butanol was further added to adjust to 500 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 500 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0038]

#### Example 7

Polymerization and evaporation under reduced pressure were carried out in a similar manner to Example 1, except that 255 kg of

acrylic acid and 75 kg of n-butyl acrylate were used instead of the monomer used in Example 1. After that, the reaction solution was kept at a temperature of 60°C, and 48% sodium hydroxide aqueous solution was added over a period of 4 hours to neutralize. When the neutralized reaction solution was analyzed, 400 ppm of n-butanol was detected. N-butanol was further added to adjust to 11,000 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 7, and 11,000 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0039]

Table 1

|                                                                  | Example |      |      |       |      |      |       |
|------------------------------------------------------------------|---------|------|------|-------|------|------|-------|
|                                                                  | 1       | 2    | 3    | 4     | 5    | 6    | 7     |
| (Meth)acrylic acid based copolymer (Type)                        | E1      | E2   | E3   | E4    | E5   | E6   | E7    |
| Acrylic acid (kg)                                                | 255     | 290  | 230  | 270   | 290  | 255  | 255   |
| N-butyl acrylate (kg)                                            | 75      |      | 100  | 60    |      | 75   | 75    |
| Isobutyl acrylate (kg)                                           |         |      |      |       | 40   |      |       |
| 2-Ethylhexyl acrylate (kg)                                       |         | 40   |      |       |      |      |       |
| Methyl acrylate (kg)                                             |         |      |      |       |      |      |       |
| Ethyl acrylate (kg)                                              |         |      |      |       |      |      |       |
| Lauryl acrylate (kg)                                             |         |      |      |       |      |      |       |
| Weight average molecular weight (Mw)                             | 6000    | 6500 | 5800 | 6400  | 6500 | 6000 | 6000  |
| Alcohol content (ppm)                                            |         |      |      |       |      |      |       |
| N-butyl alcohol (ppm)                                            | 1500    |      | 800  | 5000  |      | 500  | 11000 |
| Isobutyl alcohol (ppm)                                           |         |      |      |       | 2000 |      |       |
| 2-Ethylhexyl alcohol (ppm)                                       |         | 3000 |      |       |      |      |       |
| Ratio of alcohol based on (meth)acrylic acid based polymer (ppm) | 3750    | 7500 | 2000 | 12500 | 5000 | 1250 | 27500 |
| pH                                                               | 6       | 6    | 6    | 7     | 6    | 6    | 7     |
| Solid content concentration (% by weight)                        | 40      | 40   | 40   | 40    | 40   | 40   | 40    |
| Performance                                                      |         |      |      |       |      |      |       |
| Fluidity during wet grinding                                     | A       | A    | A    | A     | A    | A    | A     |
| Slurry temperature immediately after wet grinding (oC)           | 79      | 81   | 80   | 79    | 80   | 83   | 82    |
| Collected amount of slurry (g)                                   | 380     | 390  | 360  | 390   | 380  | 360  | 400   |
| Average diameter in the slurry (μm)                              | 0.67    | 0.67 | 0.66 | 0.67  | 0.66 | 0.66 | 0.67  |
| Temporal stability (slurry viscosity)                            |         |      |      |       |      |      |       |
| Viscosity immediately after wet grinding (mPa·s)                 | 250     | 280  | 270  | 250   | 270  | 290  | 280   |
| Viscosity after a lapse of 7 days from wet grinding (mPa·s)      | 2200    | 2500 | 2500 | 2200  | 2400 | 2900 | 2600  |

[0040]

## Comparative Example 1

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 255 kg of acrylic acid and 75 kg of methyl acrylate were

used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 350 ppm of methanol was detected. Since an alcohol having 4 to 8 carbon atoms was not detected, n-butanol was further added to adjust to 1,500 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 1,500 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0041]

#### Comparative Example 2

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 255 kg of acrylic acid and 75 kg of ethyl acrylate were used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 350 ppm of ethanol was detected. Since an alcohol having 4 to 8 carbon atoms was not detected, n-butanol was further added to adjust to 1,500 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 1,500 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0042]

#### Comparative Example 3

Polymerization, evaporation under reduced pressure, and neutralization were tried in a similar manner to Example 1, except that 255 kg of acrylic acid and 75 kg of lauryl acrylate were used instead of the monomer used in Example 1. However, since a homogenous solution could not be obtained, evaluation of the product was cancelled.

[0043]

#### Comparative Example 4

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 290 kg of acrylic acid and 40 kg of n-butyl acrylate were used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 100 ppm of n-butanol was detected.

Thus n-butanol was further added to adjust to 300 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 300 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0044]

#### Comparative Example 5

Polymerization, evaporation under reduced pressure, and neutralization were carried out in a similar manner to Example 1, except that 290 kg of acrylic acid and 40 kg of n-butyl acrylate were used instead of the monomer used in Example 1. When the neutralized reaction solution was analyzed, 100 ppm of n-butanol was detected. Thus n-butanol was further added to adjust to 13,000 ppm. In this way, a pigment dispersant having a solid content concentration of 40% by weight, a pH of 6, and 13,000 ppm of n-butanol was obtained. Measured Mw and results of wet grinding were shown in Table 1.

[0045]

Table 2

|                                                                  | Comparative Example |      |                      |      |       |
|------------------------------------------------------------------|---------------------|------|----------------------|------|-------|
|                                                                  | 1                   | 2    | 3                    | 4    | 5     |
| (Meth)acrylic acid based copolymer (Type)                        | C1                  | C2   | C3                   | C4   | C5    |
| Acrylic acid (kg)                                                | 255                 | 255  | 255                  | 290  | 290   |
| N-butyl acrylate (kg)                                            |                     |      |                      | 40   | 40    |
| Isobutyl acrylate (kg)                                           |                     |      |                      |      |       |
| 2-Ethylhexyl acrylate (kg)                                       |                     |      |                      |      |       |
| Methyl acrylate (kg)                                             | 75                  |      |                      |      |       |
| Ethyl acrylate (kg)                                              |                     | 75   |                      |      |       |
| Lauryl acrylate (kg)                                             |                     |      | 75                   |      |       |
| Weight average molecular weight (Mw)                             | 6300                | 6100 | No measurement       | 6500 | 6500  |
| Alcohol content (ppm)                                            |                     |      |                      |      |       |
| N-butyl alcohol (ppm)                                            | 1500                | 1500 | No analysis          | 300  | 13000 |
| Isobutyl alcohol (ppm)                                           |                     |      |                      |      |       |
| 2-Ethylhexyl alcohol (ppm)                                       |                     |      |                      |      |       |
| Ratio of alcohol based on (meth)acrylic acid based polymer (ppm) | 3750                | 3750 |                      | 750  | 32500 |
| pH                                                               | 6                   | 6    |                      | 6    | 6     |
| Solid content concentration (% by weight)                        | 40                  | 40   |                      | 40   | 40    |
| Performance                                                      |                     |      |                      |      |       |
| Fluidity during wet grinding                                     | C                   | C    | Evaluation incapable | C    | C     |
| Slurry temperature immediately after wet grinding (°C)           | 99                  | 97   |                      | 99   | 99    |
| Collected amount of slurry (g)                                   | 270                 | 270  |                      | 240  | 300   |
| Average diameter in the slurry (μm)                              | 0.67                | 0.67 |                      | 0.67 | 0.67  |
| Temporal stability (slurry viscosity)                            |                     |      |                      |      |       |
| Viscosity immediately after wet grinding (mPa·s)                 | 480                 | 430  |                      | 470  | 410   |
| Viscosity after a lapse of 7 days from wet grinding (mPa·s)      | 7200                | 6500 |                      | 7000 | 6600  |

[0046]

According to Examples 1 to 7 in which the pigment dispersants are consisting of a (meth)acrylic acid based copolymer using a (meth)acrylic acid alkyl ester with alkyl groups having 4 to 8 carbon atoms, and an alcohol with 4 to 8 carbon atoms, and the weight ratio of the alcohol with 4 to 8 carbon atoms is in the range from 1,000 ppm

to 30,000 ppm with respect to the (meth)acrylic acid based copolymer, it is found that the fluidity during the wet grinding was excellent, the amount of the slurry collected was large, the temperature of the slurry immediately after the wet grinding was low, and the viscosity change of the slurry of dispersion liquid through the wet grinding was small, being extremely excellent.

In contrast, according to Comparative Examples 1 and 2 in which the (meth)acrylic acid based copolymer using the (meth)acrylic acid alkyl ester with the alkyl group having carbon atoms of 3 or less is used, it is found that the fluidity during the wet grinding was inferior, the amount of the slurry collected was small, the temperature of the slurry immediately after the wet grinding was high, and the viscosity change of the slurry of the dispersion liquid through the wet grinding was large. In Comparative Example 3 in which lauryl acrylate with 12 carbon atoms is used, a homogeneous polymerization solution was not obtained.

On the other hand, according to Comparative Examples 4 and 5 in which the weight ratio of the alcohol with 4 to 8 carbon atoms relative to the (meth)acrylic acid based copolymer is not in the range from 1,000 ppm to 30,000 ppm, the fluidity during the wet grinding was inferior, the amount of the slurry collected was small, the temperature of the slurry immediately after the wet grinding was high, and the viscosity change of the slurry of the dispersion liquid through the wet grinding was large. Therefore, they are difficult to use as the pigment dispersant.

[INDUSTRIAL APPLICABILITY]

[0047]

Since the pigment dispersant obtained by the present invention contains a polymer of an acrylic acid (salt) and an acrylic acid alkyl ester with the alkyl group having 4 to 8 carbon atoms and an alcohol having specific amount of 4 to 8 carbon atoms, the dispersant adsorbs on the particles in the dispersion liquid and, at the same time, imparts smoothness between the particles and between the slurry and

the dispersion media. In the case where the pigment dispersant is used, the viscosity of the dispersion liquid can be lowered even if a pigment having a small particle size is dispersed, the increasing of the viscosity for the dispersion liquid can be reduced over time, and the amount of the slurry to be collected can be increased. In addition, there are effects such that the handling of the dispersion liquid containing the pigment dispersant of the present invention is easy and the dispersion liquid can be stored for a longer time than the conventional one. Moreover, since the exothermic heat generated at the time of wet grinding is reduced, there is also an effect that the thermal load to the apparatus upon such wet grinding is reduced.

What is Claimed is:

1. A pigment dispersant which comprises a (meth)acrylic acid based copolymer obtained using as essential components a (meth)acrylic acid monomer and a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8, and an alcohol having carbon atoms of 4 to 8,

wherein weight ratio of said alcohol having carbon atoms of 4 to 8 is in the range from 1,000 ppm to 30,000 ppm based on said (meth)acrylic acid based copolymer.

2. The pigment dispersant according to Claim 1, wherein weight ratio of said alcohol having carbon atoms of 4 to 8 is in the range from 2,000 ppm to 15,000 ppm based on said (meth)acrylic acid based copolymer.

3. The pigment dispersant according to Claim 1 or 2, wherein said (meth)acrylic acid based copolymer is obtained using 60% to 95% by weight of said (meth)acrylic acid monomer, 5% to 40% by weight of a (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8, and 0% to 10% by weight of other monomer capable of copolymerizing with said (meth)acrylic acid monomer and said (meth)acrylic acid alkyl ester monomer.

4. The pigment dispersant according to any one of Claims 1 to 3, wherein said (meth)acrylic acid alkyl ester monomer with an alkyl group having carbon atoms of 4 to 8 is a butyl (meth)acrylate, and said alcohol having carbon atoms of 4 to 8 is a butyl alcohol.

5. The pigment dispersant according to any one of Claims 1 to 4, wherein said pigment dispersant is a dispersant for wet grinding.

6. A wet grinding method of a pigment characterized in that the pigment dispersant according to any one of Claims 1 to 5 is used for the wet grinding of said pigment.