

SPECIFICATION

SURFACE-TREATED CALCIUM CARBONATE FILLER, METHOD FOR PRODUCING THE SAME, AND RESIN COMPOSITION CONTAINING THE FILLER

Technical Field

The present invention relates to a surface-treated calcium carbonate filler and method for producing the same, and resin composition containing the filler, more particularly, it relates to a surface-treated calcium carbonate filler which not only gives excellent thixotropy, excellent slump resistance and good storage stability, but also excellent heat resistance at the time of drying when applied to curing resins, which gives excellent insulation property when applied to electronic materials, and which gives excellent gloss and water resistance when applied to paints and inks, and further, method for producing it and resin composition containing the filler.

Background Art

Calcium carbonate has been widely used as a filler for paints, papers, rubbers, plastics, sealing materials, or pigments.

Among those, for example, in the case of sealing materials, calcium carbonate is in wide use for the purposes of water-proofing and sealing in the fields such as architectures, automobiles and flooring materials. In these fields, a moisture-curing one-pack

type resin composition (hereinafter referred to as one-pack resin composition) has many advantages at the time of application; it does not need mixing technique since two liquids are not required to be mixed prior to application as compared with a two-pack resin composition; it can shorten a working time, and the like. For such advantages, the Production amount rapidly increases. In the application of the one-pack resin composition, especially joint fillers and sealing materials, it is often applied to a vertical place and thus it is naturally required not to sag down from application up to curing. Accordingly, it should have high thixotropy and slump resistance, though workability upon application might be somewhat affected. In order to impart these properties, colloidal silica, calcium carbonate or the like have been hitherto used. However, these thixotropy-imparting agents have numerous drawbacks such as an increase in viscosity during storage, and foaming and cracking in the bonded interface at the time of curing of a urethane resin.

For example, in the case of colloidal silica, as shown by Japanese Examined Patent Publication (Kokoku) Nos. 45-41110 and 53-5899, many proposals have been made heretofore and its superiorities are recognized, but it includes numerous problems such as poor adaptability to an object to be bonded owing to high modulus after curing, difficulty in delicate adjustment of viscosity because of high thixotropy with a small amount, a decrease in thixotropy with a lapse of time, poor weatherability and difficulty

in handling in the viewpoint of labor hygiene because of a danger of silicosis.

In the case of calcium carbonate as well, one obtained by grinding limestone as a material and classifying the resulting powder which is generally called heavy calcium carbonate contains coarse particles and is insufficient in properties such as poor thixotropy. Although the heavy calcium carbonate is generally surface-treated with fatty acids or paraffin, since it is treated by a dry method that calcium carbonate and a surface-treating agent are stirred under heating, the entire surface of calcium carbonate is not coated so that the uncoated hydrophilic surface unavoidably remains. As a result, moisture adsorbed on the hydrophilic surface gives an adverse effect on the storage stability. Moreover, a thixotropy-imparting effect can hardly be expected.

On the other hand, in the case of precipitated calcium carbonate as well, in one-pack resin composition cured with moisture contained in air, the curing reaction starts with moisture adsorbed on the surface of the calcium carbonate. When it is surface-treated with a general surface-treating agent such as alkali metal salts of fatty acids and resin acids, surfactants such as alkylbenzenesulfonic acid and salts thereof, polymerization reaction proceeds through the reaction with moisture since it tends to adsorb moisture due to strong hydrophilic property. In either case, it becomes a cause of extreme decrease in storage stability, foaming and cracking. For this reason, it is naturally dried

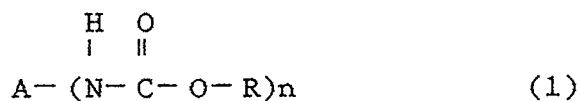
preliminarily and then used but when it is surface-treated with a hydrophilic surfactant, in particular, the removal ratio of moisture is low and moreover an influence of hydrophilic alkali metal ions is not avoidable so that the storage stability deteriorates.

In the case of modified silicone resins among sealing materials, calcium carbonate surface-treated with alkali metal salts of fatty acids is commonly used, but the removal ratio of moisture is low and thus it can not be used without use of a high expensive dehydrating agent. In Japanese Non-examined Patent Publication (Kokai) No. 2-38309, there is proposed calcium carbonate surface-treated with fatty acid esters and according to this technique, the foregoing problems are solved to some extent and an effective direction is found out in the field of a sealing material which is typical of one-pack resin compositions.

Notwithstanding, it is difficult to say that the ester bond is thermally stable and thus there is a problem with respect to heat resistance upon drying. That is, in order to increase the removal ratio of moisture, when it is heated, for example, at a temperature of not lower than 130 °C for a long period of time or at 150°C for several hours, heat deterioration takes place to thus damage properties inherent therein.

Moreover, in Japanese Non-examined Patent Publication (Kokai) No. 10-245221, there is proposed calcium carbonate surface-treated with a compound having a melting point of not lower than 50°C which

is represented by the formula (1), and at least one selected from the group consisting of carboxylic acids, sulfonic acids and metal salts thereof. However, when such surface-treated calcium carbonate is used, for example, in one-pack type polyurethane, the obtained sealant is discolored to brown, and therefore, when a whitish sealant is intended, an expensive colorant must be used. In addition, since curing is slow, deposition of dirt on the surface of sealant after application up to curing becomes problematic.



wherein A is a residual group eliminating an isocyanate group from an isocyanate compound or a residual group eliminating an amino group from an amino compound, n is an integer of 1 to 4, and R is a hydrocarbon group in which at least one of R is a hydrocarbon group having carbon atoms of not less than 8.

Furthermore, in the field of resin compositions such as plastics, paints and inks, calcium carbonate has been in use as fillers or pigments. As calcium carbonate used in resin compositions such as plastics, paints and inks, both types called heavy calcium carbonate and precipitated calcium carbonate are used. These are often used as surface-treated with alkali metal salts of fatty acids, alkali metal salts of resin acids and fatty acid esters. When calcium carbonate surface-treated with alkali metal salts of

fatty acids, alkali metal salts of resin acids and fatty acid esters is used, for example, in plastics, dispersibility is sometimes poor. Moreover, when it is used in the field requiring insulation property such as electric wires, the practically usable performance is obtained. But, more improved insulation property is demanded and it is the real state that, for example, in the case of condenser film, it can not be used because of insufficient insulation property. Furthermore, when it is used in paints or inks, the practically usable performance is obtained, but the fact is that more improved properties such as water resistance are waited.

In light of the foregoing situation, the present invention provides a surface-treated calcium carbonate filler which not only gives excellent thixotropy, excellent slump resistance and good storage stability, but excellent heat resistance at the time of drying when applied to curing resin compositions, which gives excellent dispersibility and excellent insulation property when applied to plastics, and which gives excellent gloss and excellent water resistance when applied to paints and inks, and method for producing it and resin composition containing the filler.

The present inventors have made an extensive series of studies in an attempt to solve the foregoing problems and found out that the specific surface-treated calcium carbonate filler and the resin composition containing the surface-treated calcium carbonate filler attain the intended objects, and thus have completed the present invention.

Disclosure of Invention

The present invention is, in a first aspect, to provide a surface-treated calcium carbonate filler, in which the surface of calcium carbonate is wet-surface-treated with at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids (Claim 1).

The present invention is, in a second aspect, to provide a surface-treated calcium carbonate filler, in which the surface of calcium carbonate is wet-surface-treated with at least one surface-treating agent selected from the group consisting of metallic soaps of saturated fatty acids, metallic soaps of unsaturated fatty acids, metallic soaps of alicyclic carboxylic acids and metallic soaps of resin acids, and a content of alkali metals is not more than 1.0×10^{-3} mol/100 g CaCO_3 (Claim 2).

The preferred embodiment is a surface-treated calcium carbonate filler of Claim 1 or 2, wherein a BET specific surface area of the calcium carbonate is 3 to 120 m^2/g (Claim 3).

The present invention is, in a third aspect, to provide a method for producing the surface-treated calcium carbonate filler of Claim 1 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic

carboxylic acids and resin acids, and

heating the resulting mixture to a temperature of not lower than a melting point of these acids to thereby surface-treating the calcium carbonate (Claim 4).

The present invention is, in a fourth aspect, to provide a method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, (A) at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, and (B) a metallic hydroxide or a metallic oxide which is capable of producing a water-insoluble metallic soap through the reaction with (A), and

surface-treating the calcium carbonate with a metallic soap of (A) obtained through the reaction of (A) and (B) (Claim 5).

The present invention is, in a fifth aspect, to provide a method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of a metallic soap of saturated fatty acids, a metallic soap of unsaturated fatty acids, a metallic soap of alicyclic carboxylic acids and a metallic soap of resin acids in an organic solvent slurry,

dehydrating and drying the resulting slurry, and

heating the resulting mixture to a temperature of not lower than a melting point of the metallic soap added to thereby surface-treat the calcium carbonate (Claim 6).

The present invention is, in a sixth aspect, to provide a method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids,

surface-treating the calcium carbonate with the surface-treating agent, and

washing the treated calcium carbonate with water to thereby control a content of alkali metals to not more than 1.0×10^{-3} mol/100 g CaCO_3 (Claim 7).

The present invention is, in a seventh aspect, to provide a method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids,

surface-treating the calcium carbonate with the surface-

treating agent,

adding a metallic compound which is capable of producing a metallic soap through the reaction with the alkali metal salts of (C) to thereby conduct double decomposition to a metallic soap of (C), and

washing the treated calcium carbonate with water to thereby control a content of alkali metals to not more than 1.0×10^{-3} mol/100 g CaCO_3 (Claim 8).

The present invention is, in an eighth aspect, to provide a resin composition comprises blending with a resin the surface-treated calcium carbonate filler of any one of Claims 1 to 3 (Claim 9).

The preferred embodiment is a resin composition of Claim 9, wherein the resin is a resin in use for paints (Claim 10).

The preferred embodiment is a resin composition of Claim 9, wherein the resin is a resin in use for inks (Claim 11).

The preferred embodiment is a resin composition of Claim 9, wherein the resin is a resin in use for plastics (Claim 12).

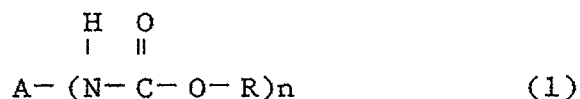
The preferred embodiment is a resin composition of Claim 9, wherein the resin is a resin in use for sealants (Claim 13).

The preferred embodiment is a resin composition of Claim 9, wherein the resin is a curing resin (Claim 14).

The preferred embodiment is a resin composition of Claim 9, wherein the resin is a moisture-curing resin (Claim 15).

The present invention is, in a ninth aspect, to provide a

moisture-curing resin composition comprises blending with a resin the surface-treated calcium carbonate filler of any one of Claims 1 to 3, and (D) calcium carbonate surface-treated with a fatty acid ester and/or a compound having a melting point of not lower than 50 °C which is represented by the following formula (1) and at least one selected from the group consisting of carboxylic acids, sulfonic acids, and metal salts thereof (Claim 16).



wherein A is a residual group eliminating an isocyanate group from an isocyanate compound or a residual group eliminating an amino group from an amino compound, n is an integer of 1 to 4, R is a hydrocarbon group in which at least one of R is a hydrocarbon group having carbon atoms of not less than 8.

Best Mode for Carrying Out the Invention

The surface-treating agents used in the present invention are saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids, resin acids or metallic soaps thereof (In the present specification, metallic soaps mean metallic salts other than alkali metals.) and these are used singly or in combination of two or more.

These surface-treating agents are not surfactants and thus hydrophobic. These are coated by a wet-treating method in every nook and cranny of the surface of calcium carbonate. Thus, these surface-treating agents are excellent in dispersibility in a variety of resins and thermally stable as compared with fatty acid esters and thus the calcium carbonate surface-treated therewith are also high in thermal stability. Accordingly, it can be dried at a high temperature and, for example, in the case of one-pack modified silicone sealants, there is a merit that use of an expensive dehydrating agent is omitted. Further, it is also useful as a filler for rapid curing sealants and for the adjustment of curing time. Furthermore, when the surface-treated calcium carbonate of the present invention is applied, for example, to a condenser film, excellent dispersibility and insulation property are exhibited, and when applied, for example, to paints and inks, excellent water resistance is exhibited.

The surface-active calcium carbonate filler is produced by the following methods.

The first method comprises adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, heating the resulting mixture to a temperature of not lower than a melting point of these acids, and stirring the mixture, followed by dehydrating, drying and grinding by usual methods.

The second method comprises adding to an aqueous slurry containing calcium carbonate, (A) at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, and (B) a metallic hydroxide or a metallic oxide which is capable of producing a metallic soap through the reaction with (A), surface-treating the calcium carbonate with a metallic soap of (A) obtained through the reaction of (A) and (B), followed by dehydrating, drying and grinding by usual methods. The time for adding (B) may be before or after (A) is added, and may be concurrent with (A).

As the metallic hydroxide producing a metallic soap through the reaction with at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, barium hydroxides, calcium hydroxides, magnesium hydroxides and strontium hydroxides are exemplified, and as the metallic oxide producing a metallic soap through the reaction with (A), barium oxides, calcium oxides, magnesium oxides and strontium oxides are exemplified. These are used singly or in combination of two or more.

The third method comprises adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of metallic soaps of saturated fatty acids, metallic soaps of unsaturated fatty acids, metallic soaps of alicyclic carboxylic acids and metallic soaps of resin acids, and stirring the resulting mixture vigorously to thereby

surface-treat the calcium carbonate. These metallic soaps have a strong water repellency and do not have compatibility with water and thus it is preferred to add in a form of slurry of a water-soluble organic solvent.

As the water-soluble organic solvent, alcohols such as methyl alcohol, ethyl alcohol and propyl alcohol; ketones such as ethyl methyl ketone, methyl propyl ketone are exemplified and these may be used singly or in combination of two or more. The metallic soaps used herein should desirably be as fine as possible from the viewpoint of obtaining the uniform coating. Moreover, it becomes more complete if the heat-treatment is conducted at a temperature of not lower than the melting point of the metallic soaps used after dehydrating and drying.

The fourth method comprises adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids, surface-treating the calcium carbonate with the surface-treating agent, and washing the treated calcium carbonate with water to thereby control the content of alkali metals to not more than 1.0×10^{-3} mol per 100 g of CaCO_3 . What is important in this method is that as alkali metals pose problems with respect to the storage stability due to their hydrophilic property, it is required to substitute alkali metals contained in

(C) with calcium to thus form a calcium soap of saturated fatty acids, a calcium soap of unsaturated fatty acids, a calcium soap of alicyclic carboxylic acids and a calcium soap of resin acids, and as a result, washing the alkali ions liberated with water to thereby control the content of the alkali metals to not more than 1.0×10^{-3} mol per 100 g of CaCO_3 .

The fifth method comprises adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids, surface-treating the calcium carbonate with the surface-treating agent, and adding a metallic compound which produces a metallic soap through the reaction with the alkali metal salts of (C) to thereby conduct double decomposition to produce a metallic soap of (C). In this method as well, for the same reasons as in the fourth method, it is necessary to wash alkali metals with water to a level of not more than 1.0×10^{-3} mol per 100 g of CaCO_3 . If the content of alkali metals is more than 1.0×10^{-3} mol, the storage stability becomes insufficient.

As the metallic compound producing a metallic soap through the reaction with (C), chlorides such as aluminium chloride, calcium chloride, ferric chloride, magnesium chloride, lead chloride and zinc chloride; sulfates such as magnesium sulfate and aluminium sulfate are exemplified, and these are used singly or in

combination of two or more.

The above-mentioned five methods are carried out singly or in combination of two or more.

Although the saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids used in the present invention are not limited specifically, those having as many carbon atoms as possible are preferred to use. For example, when used in curing type resins, it is preferable to use those having carbon atoms of not less than 8 since, besides storage stability, high thixotropy and slump resistance are satisfied.

For example, the saturated fatty acids such as caprilic acid, lauric acid, myristic acid, palmitic acid, stearic acid and arachic acid; unsaturated fatty acids such as oleic acid, elaidic acid, linoleic acid and ricinolic acid; alicyclic carboxylic acids such as naphthenic acid; resin acids such as abietic acid, pimaric acid, palustric acid and neoabietic acid are exemplified. As the metallic soaps of these acids, metallic soaps of Ag, Al, Ba, Ca, Cu, Fe, Mg, Mn, Pb, Sn, and Zn are exemplified and these are used singly or in combination of two or more.

The amount of the surface-treating agent is not specifically limited, but the range of 0.1 to 20.0 parts by weight per 100 parts by weight of calcium carbonate is preferable. If it is less than 0.1 part by weight, effects of the surface-treating are sometimes insufficient, and even if it is more than 20.0 parts by weight, more prominent effects are not expected and thus sometimes uneconomical.

As the content of the alkali metals, the intended purpose of the present invention is can be attained if it is not more than 1.0×10^{-3} mol/100 g CaCO_3 , but intended purpose of the present invention is attained more efficiently as it becomes smaller. Therefore, it is preferably not more than 7.0×10^{-4} mol/100 g CaCO_3 , more preferably not more than 5.0×10^{-4} mol/100 g CaCO_3 .

The calcium carbonate used in the present invention is not limited specifically but selected from the intended properties of resin compositions. For example, it is optionally possible to select according to the purpose, heavy calcium carbonate obtained by grinding limestone as a material and classifying the resulting powder to a desired particle size, precipitated calcium carbonate produced by calcining limestone to prepare quick lime, preparing an aqueous slurry of slaked lime by hydrating, passing carbon dioxide gas through the slurry, and solution method calcium carbonate obtained by the reaction of a carbonate solution with a calcium salt solution. For example, to obtain high thixotropy and excellent slump resistance used for curing type resin compositions, calcium carbonate preferably having a BET specific surface area of 3 to $120 \text{ m}^2/\text{g}$, more preferably 5 to $100 \text{ m}^2/\text{g}$ is used. If it is less than $3 \text{ m}^2/\text{g}$, it is difficult to impart high viscosity, and if it is more than $120 \text{ m}^2/\text{g}$, it is necessary to increase the amount of the surface-treating agent to cover the hydrophilic surface and thus this results in high cost and is not preferable. It is more preferable to use the precipitated calcium carbonate which is

capable of obtaining a higher BET specific surface area. Moreover, when the heavy calcium carbonate is used as the surface-treated calcium carbonate filler, as it is mechanically ground and classified, the content of alkali metals contained therein is small and the surface activity is low so that it is excellent in removal ratio of moisture. For this reason, when used in curing resin compositions, it is advantageous in storage stability.

The surface-treated calcium carbonate filler of the present invention is excellent in dispersibility, in particular, and thus it is suited for a variety of resins. For example, when used in curing type resins for sealing materials, adhesives, flooring materials, excellent thixotropy and slump resistance and storage stability are provided, when used in paints and inks, excellent gloss and water resistance are provided, and when used in plastics, excellent mechanical strength and thermal stability are provided. Further, when used in films among plastics, excellent anti-blocking property and insulation property are provided, and it is especially effective when used in condenser films.

The resins with which the surface-treated calcium carbonate filler of the present invention is blended are not specifically limited and examples are liquid resins such as polyurethane, polysulfide, silicone, modified silicone and polyisobutylene for sealing materials; liquid resins such as urea resin, phenolic resin, epoxy resin, silicone resin and acrylic resin for adhesives; liquid resins such as epoxy resin, polyurethane resin and polyester resin

for flooring materials; liquid resins such as phenolic resin, alkyd resin, unsaturated polyester resin, amino resin, epoxy resin, polyvinyl resin, acrylic resin, polyurethane resin, silicone resin and fluororesin for paints; rosin, phenolic resin, alkyd resin, polyamide resin, polyurethane resin, epoxy resin, polyester resin and acrylic resin for inks; thermosetting resins such as phenolic resin, urea resin, melamine resin, unsaturated polyester resin, epoxy resin, polyurethane resin and polyimide resin for plastics; thermoplastic resins such as polyvinyl chloride resin, polyethylene resin, polypropylene resin, polystyrene resin, ABS resin, polyamide resin, polyacetal resin, polycarbonate resin, fluororesin and polyethylene terephthalate resin. These are used singly or in combination of two or more.

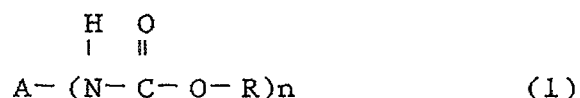
The amount of the surface-treated calcium carbonate filler of the present invention blended with the resin is variable depending upon the kind of resins and use of the resin compositions, but is usually about 20 to about 200 parts by weight based on 100 parts by weight of resin, preferably about 40 to about 150 parts by weight.

If it is less than 20 parts by weight, sufficient thixotropy is not imparted, and if it is more than 200 parts by weight, the viscosity becomes too high to worsen workability.

The resin compositions of the present invention may further include for the purpose of adjusting other properties, other fillers such as colloidal silica, talc, kaolin, zeolite, resin balloon and glass balloon; plasticizers such as dioctyl phthalate and dibutyl

phthalate; solvents such as aromatic hydrocarbons like toluene and xylene, aliphatic hydrocarbons like hexane and butane; oil solvents such as gasoline; ethers or esters such as ketones like acetone, methyl ethyl ketone and Cellosolve acetate; additives such as silicone oil and fatty acid-modified silicone oil, and other various additives and colorants, singly or in combination of two or more.

When the surface-treated calcium carbonate filler of the present invention is used, for example, in moisture-curing resin compositions, it is possible to adjust the curing speed of the resin composition by the conjoint use of fillers conventionally used. In the moisture-curing resin compositions, calcium carbonate surface-treated with a fatty acid ester and/or a compound having a melting point of not lower than 50°C which is represented by the following formula (1) and at least one selected from the group consisting of carboxylic acids, sulfonic acids, and metal salts thereof:



wherein A is a residual group eliminating an isocyanate group from an isocyanate compound or a residual group eliminating an amino group from an amino compound, n is an integer of 1 to 4, R is a hydrocarbon group in which at least one of R is a hydrocarbon group having carbon atoms of not less than 8.

The conventional surface-treated calcium carbonate filler used in the moisture-curing resin compositions exhibits storage stability necessary for the moisture-curing resin compositions but it can not be said that the curing time is short, and thus it must rely upon the adjustment of the amount of a catalyst. However, it is possible to shorten the curing time through an improvement of a drawback of the curing time being long which is associated with the conventional surface-treated calcium carbonate filler by using the surface-treated calcium carbonate filler of the present invention in combination with the conventional filler.

The proportion of the surface-treated calcium carbonate filler of the present invention with the conventional filler is not specifically limited and it is optionally determined so that the curing time becomes a desired level.

Hereinafter, the present invention will be explained in more detail by way of examples and comparative examples but the present invention is in no way limited thereby.

Example 1

To 10 Kg of an aqueous slurry containing precipitated calcium carbonate having a BET specific surface area of $20 \text{ m}^2/\text{g}$, controlled to 160 g of CaCO_3/kg water in concentration and controlled to 75°C , 80 g of stearic acid (melting point 70°C) were added and stirred for one hour to thereby conduct the surface-coating. Thereafter, the resulting mixture was dehydrated to a solid content of 60% by weight, then dried and ground to thereby obtain a calcium carbonate

powder surface-treated with stearic acid.

Example 2

The same procedure was carried out in the same manner as in Example 1 except that stearic acid was changed to lauric acid (melting point 44 °C) and that 75 °C was changed to 50°C.

Example 3

To 10 Kg of an aqueous slurry containing precipitated calcium carbonate having a BET specific surface area of 20 m²/g, controlled to 160 g of CaCO₃/kg water in concentration and controlled to 75°C, 80 g of stearic acid were first added, then 104.2 g of a 10% by weight calcium hydroxide slurry were added and stirred for 5 hours to thereby conduct the surface-coating. Thereafter, the resulting mixture was dehydrated to solid content of 60% by weight, then dried and ground to thereby obtain a calcium carbonate powder surface-treated with calcium stearate.

Example 4

The same procedure was carried out in the same manner as in Example 3 except that 104.2 g of the 10% by weight calcium hydroxide slurry were changed to 15.8 g of calcium oxide to thereby obtain a calcium carbonate powder surface-treated with calcium stearate.

Example 5

The same procedure was carried out in the same manner as in Example 3 except that the stearic acid was changed to lauric acid, that 75°C was changed to 50°C, and that the amount of calcium hydroxide slurry was changed from 104.2 g to 148 g to thereby

obtain a calcium carbonate powder surface-treated with calcium laurate.

Example 6

To 10 Kg of an aqueous slurry containing precipitated calcium carbonate having a BET specific surface area of $20 \text{ m}^2/\text{g}$, controlled to 160 g of CaCO_3/kg water in concentration and controlled to 75°C , 800 g of a 10% by weight methanol slurry containing magnesium stearate (melting point 132°C) were added and stirred for one hour to thereby conduct the surface-coating. Thereafter, the resulting mixture was dehydrated to a solid content of 60% by weight, then dried and, after heat-treating for one hour at 140°C , ground to thereby obtain a calcium carbonate powder surface-treated with magnesium stearate.

Example 7

The same procedure was carried out in the same manner as in Example 5 except that the magnesium stearate was changed to magnesium laurate (melting point 150°C) and that 140°C was changed to 160°C .

Example 8

To 10 Kg of an aqueous slurry containing precipitated calcium carbonate having a BET specific surface area of $20 \text{ m}^2/\text{g}$, controlled to 160 g of CaCO_3/kg water in concentration and controlled to 75°C , 800 g of a 10% by weight hot water solution containing potassium stearate were added and stirred for one hour to thereby conduct the surface-coating. Thereafter, the resulting mixture was diluted

with water 5-fold with stirring and dehydrated to a solid content of 60% by weight, then dried and ground to thereby obtain a calcium carbonate powder surface-treated with calcium stearate. The amount of potassium was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was 5.2×10^{-4} mol/100g CaCO_3 .

Example 9

The same procedure was carried out as in the same manner as in Example 8 except that the dilution with water was changed from 5-fold to 2-fold. The amount of potassium contained in the obtained calcium carbonate powder surface-treated with calcium stearate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was 8.5×10^{-4} mol/100g CaCO_3 .

Example 10

The same procedure was carried out in the same manner as in Example 8 except that 800 g of the 10% by weight hot water solution containing potassium stearate was changed to 800 g of a 10% by weight hot water solution containing potassium abietate. The amount of potassium contained in the obtained calcium carbonate powder surface-treated with calcium abietate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was 5.0×10^{-4} mol/100g CaCO_3 .

Example 11

To 10 Kg of an aqueous slurry containing precipitated calcium carbonate having a BET specific surface area of $20 \text{ m}^2/\text{g}$, controlled

to 160 g of CaCO_3 /kg water in concentration, 800 g of a 10% by weight hot water solution containing potassium stearate were added, then 236 g of a 10% by weight magnesium chloride slurry were added and stirred for 5 hours to thereby conduct the surface-coating. Thereafter, the resulting mixture was diluted with water 5-fold with stirring and dehydrated to a solid content of 60% by weight, then dried and ground to thereby obtain a calcium carbonate powder surface-treated with magnesium stearate. The amount of potassium contained in the obtained surface-treated calcium carbonate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $4.1 \times 10^{-4} \text{ mol/100g CaCO}_3$.

Example 12

An aqueous slurry containing heavy calcium carbonate having a BET specific surface area of $2 \text{ m}^2/\text{g}$, controlled to 200 g of CaCO_3 /kg water in concentration was wet-ground by the use of a wet-grinder and an aqueous slurry containing heavy calcium carbonate having a BET specific surface area of $15 \text{ m}^2/\text{g}$ was obtained. To 10 Kg of the obtained aqueous slurry, 800 g of a 10% by weight hot water solution containing potassium stearate were added to thereby conduct the surface-coating. Thereafter, the resulting mixture was diluted with water 5-fold with stirring and dehydrated to a solid content of 60% by weight, then dried and ground to thereby obtain a calcium carbonate powder surface-treated with calcium stearate. The amount of potassium contained in the obtained surface-treated calcium carbonate was measured by an X-ray fluorescence analyzer (XFR-1500

manufactured by Shimadzu Corp.) and its result was 2.5×10^{-4} mol/100g CaCO_3 .

Comparative Example 1

8 Kg of precipitated calcium carbonate powder comprising the non-surface-treated precipitated calcium carbonate prepared in Example 1 were charged into a 20-liter Supermixer (SMV-20 type, stirring blades: two blades of S type and BL type, manufactured by Kawata Seisakusyo) and heated to 90°C , then 400 g of stearic acid were charged and mixed at 2000 rpm for 30 minutes to conduct the surface-treating by a dry method, and thus a calcium carbonate powder dry-surface-treated with stearic acid was obtained.

Comparative Example 2

The same procedure was carried out in the same manner as in Example 1 except that 75°C was changed to 50°C .

Comparative Example 3

The same procedure was carried out in the same manner as in Example 3 except that 104.2 g of the 10% by weight calcium hydroxide slurry were changed to 157.7 g of a 10% by weight potassium hydroxide solution.

Comparative Example 4

The same procedure was carried out in the same manner as in Example 6 except that the heat-treatment for one hour at 140°C was changed to the heat-treatment for one hour at 120°C .

Comparative Example 5

The same procedure was carried out in the same manner as in

Example 8 except that the dilution with water of 5-fold with stirring was not conducted (without dilution). The amount of potassium contained in the obtained calcium carbonate powder surface-treated with calcium stearate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $2.0 \times 10^{-3} \text{ mol/100g CaCO}_3$.

Comparative Example 6

The same procedure was carried out in the same manner as in Example 1 except that the stearic acid was changed to sodium stearate. The amount of sodium contained calcium carbonate powder surface-treated with calcium stearate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $2.2 \times 10^{-3} \text{ mol/100g CaCO}_3$.

Comparative Example 7

The same procedure was carried out as in the same manner as in Example 1 except that the stearic acid was changed to sodium laurate. The amount of sodium contained calcium carbonate powder surface-treated with calcium laurate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $3.0 \times 10^{-3} \text{ mol/100g CaCO}_3$.

Comparative Example 8

The same procedure was carried out in the same manner as in Example 10 except that the dilution with water of 5-fold with stirring was not conducted (without dilution). The amount of potassium contained in the obtained calcium carbonate powder

surface-treated with calcium stearate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $2.1 \times 10^{-3} \text{ mol/100g CaCO}_3$.

Comparative Example 9

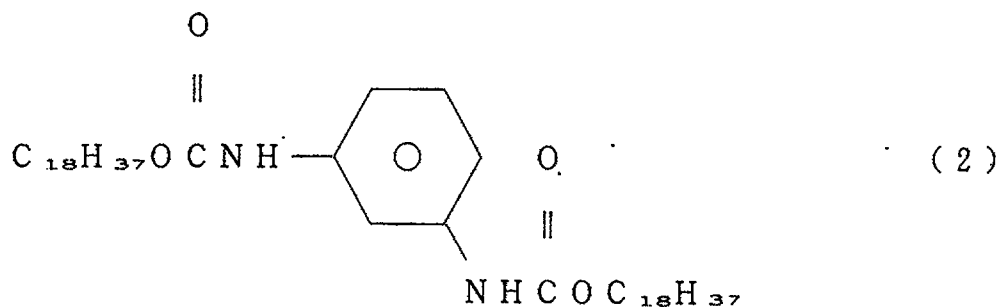
The same procedure was carried out in the same manner as in Example 11 except that the dilution with water of 5-fold with stirring was not conducted (without dilution). The amount of potassium contained in the obtained calcium carbonate powder surface-treated with magnesium stearate was measured by an X-ray fluorescence analyzer (XFR-1500 manufactured by Shimadzu Corp.) and its result was $1.9 \times 10^{-3} \text{ mol/100g CaCO}_3$.

Comparative Example 10

The same procedure was carried out in the same manner as in Example 1 except that the stearic acid was changed to stearyl glycerin ester.

Comparative Example 11

To 1 Kg of the calcium carbonate powder surface-treated with sodium laurate, 50 g of a surface-treating agent having an average diameter of $30 \mu \text{ m}$ represented by the formula (2) were added and the dry-surface-treatment was conducted by the use of a Nauta mixer at room temperature for 15 minutes and at 110°C for one hour.



Examples 13 to 23, Comparative Examples 12 to 22

The powders obtained by Examples 1 to 9, 11, 12 and Comparative Examples 1 to 7, 9 to 11 were dried at 150°C for 5 hours and modified silicone one-pack type sealing material compositions were prepared by the following blending ratios and the kneading method and the properties were evaluated by the following tests. Meanwhile, in Comparative Example 21 the powder was dried at 120 °C for 5 hours. The results are shown in Table 1.

[Blending ratios]

Resin (MS polymer S203 manufactured by Kaneka Corporation)

50 parts by weight

Plasticizer DOP

50 parts by weight

Samples: surface-treated calcium carbonate filler

120 parts by weight

Catalyst (NEOSTANN U220 manufactured by Nitto Kasei Co., Ltd.)

2 parts by weight

[Kneading method]

The above-mentioned compositions were kneaded by the use of an undersize kneader to prepare sealing materials. The sealing

materials thus obtained were tightly packed into a cylindrical cartridge for one-pack type sealing materials.

[Storage stability test]

Evaluation was made by viscosity immediately after kneading (20 °C x 1 day) and after lapse of time (50°C x 2 weeks in an oven).

[Measurement method of viscosity]

Measurement was made by the use of a B8U type viscometer (rotor: No.7).

[Slump resistance]

The state in which the sealing materials were applied vertically was evaluated with naked eyes according to the following criteria:

- : good
- △ slightly bad
- × bad

Table 1

	Items Samples	Color of powder before drying	Color of powder after drying	Storage stability (Oven at 50°C) (×10 ⁴ cP)						Slump resistance
				Immediately after kneading (20°C×1 day)			After two weeks			
				1 rpm	1 Orpm	1 rpm/1 Orpm	1 rpm	1 Orpm	1 rpm/1 Orpm	
Example 13	Example 1	White	White	855	103.0	8.30	1030	138	7.46	○
Example 14	Example 2	White	White	680	84.5	8.05	782	112	6.98	○
Example 15	Example 3	White	White	838	99.0	8.46	1050	140	7.50	○
Example 16	Example 4	White	White	822	96.1	8.55	1030	138	7.46	○
Example 17	Example 5	White	White	735	90.4	8.13	1035	159	6.51	○
Example 18	Example 6	White	White	808	96.4	8.38	1091	143	7.63	○
Example 19	Example 7	White	White	708	86.4	8.19	891	143	6.28	○
Example 20	Example 8	White	White	849	97.6	8.70	1102	154	7.16	○
Example 21	Example 9	White	White	852	99.7	8.55	1520	216	7.04	○
Example 22	Example 11	White	White	851	95.2	8.94	1150	157	7.32	○
Example 23	Example 12	White	White	375	62.1	6.04	551	108	5.10	○
Comp. Ex. 12	Comp. Ex. 1	White	White	176	44.2	3.98	Unmeasurable	Unmeasurable	—	×
Comp. Ex. 13	Comp. Ex. 2	White	White	185	41.9	4.42	Unmeasurable	Unmeasurable	—	×
Comp. Ex. 14	Comp. Ex. 3	White	White	705	102.5	6.88	Unmeasurable	Unmeasurable	—	○
Comp. Ex. 15	Comp. Ex. 4	White	White	354	60.5	5.85	Unmeasurable	Unmeasurable	—	△
Comp. Ex. 16	Comp. Ex. 5	White	White	844	98.1	8.60	Unmeasurable	Unmeasurable	—	○
Comp. Ex. 17	Comp. Ex. 6	White	White	827	96.5	8.57	Unmeasurable	Unmeasurable	—	○
Comp. Ex. 18	Comp. Ex. 7	White	White	665	95.9	6.93	Unmeasurable	Unmeasurable	—	×
Comp. Ex. 19	Comp. Ex. 9	White	White	831	98.3	8.45	Unmeasurable	Unmeasurable	—	×
Comp. Ex. 20	Comp. Ex. 10	White	Yellowish brown	258	51.2	5.04	314	46.5	6.90	×
Comp. Ex. 21	Comp. Ex. 10	White	White	910	103.0	8.83	2030	308	6.60	○
Comp. Ex. 22	Comp. Ex. 11	Yellow	Yellowish brown	790	91.2	8.66	1503	220	6.82	○

It is apparent from Table 1 that the compositions containing the surface-treated calcium carbonate fillers of the present invention are superior in storage stability, thixotropy and slump resistance.

Examples 24 to 42, Comparative Examples 23 to 35

The powders obtained by Examples 1 to 9, 11, 12, and Comparative Examples 1 to 7, 9 to 11 were dried at 150 °C for 5 hours and urethane one-pack type sealing material compositions were prepared by the following blending ratios and the kneading method and the properties were evaluated by the following tests. Meanwhile, in Comparative Example 32 the powder was dried at 120°C for 5 hours. The results are shown in Table 2.

In addition, the pot life one-pack type urethane sealing materials was measured varying the blending ratios of the surface-treated calcium carbonate fillers obtained in Examples 3, 4 and Comparative Examples 10, 11. The results are shown in Table 3.

[Blending ratios]

Resin (TAKENATE L1078 manufactured by Takeda Chemical Industries, Ltd.)

120 parts by weight

Samples:surface-treated calcium carbonate filler 80 parts by weight

[Kneading method]

The above-mentioned compositions were kneaded by the use of an undersize kneader to prepare sealing materials. The sealing materials thus obtained were tightly packed into a cylindrical cartridge for one-pack type sealing materials.

[Storage stability test]

Evaluation was made by viscosity immediately after kneading (20 °C x 1 day) and after lapse of time (40°C x 2 weeks in an oven).

[Measurement method of viscosity]

Measurement was made by the use of a B8U type viscometer (rotor: No.7).

[Slump resistance]

The state in which the sealing materials were applied vertically was evaluated with naked eyes according to the following criteria:

○: good

△: slightly bad

×: bad

[Curing property]

Evaluation was made by time required for the sealing materials to cure to such a degree that it does not adhere to a finger at 20 °C after extruded from the cartridge.

○: Curing is completed within 3 hours.

×: Curing is not completed within 3 hours.

[Curing time]

Time was measured which required for the sealing materials to cure to such a degree that it does not adhere to a finger at 20 °C after extruded from the cartridge.

Table 2

	Items Samples	Color of powder before drying	Color of powder after drying	Storage stability (Oven at 40°C) (×10 ⁴ cP)						Slump resistance	Curing property
				Immediately after kneading (20°C×1 day)			After two weeks				
				2.5rpm	20rpm	2.5rpm/20rpm	2.5rpm	20rpm	2.5rpm/20rpm		
Example 24	Example 1	White	White	300	41.0	7.21	322	49.5	6.51	○	○
Example 25	Example 2	White	White	285	40.8	6.99	303	46.5	6.52	○	○
Example 26	Example 3	White	White	352	47.4	7.43	388	56.5	6.87	○	○
Example 27	Example 4	White	White	349	47.2	7.37	377	56.2	6.71	○	○
Example 28	Example 5	White	White	352	48.7	7.23	401	67.8	5.91	○	○
Example 29	Example 6	White	White	355	49.1	7.23	397	67.2	5.91	○	○
Example 30	Example 7	White	White	316	44.9	7.04	325	48.6	6.69	○	○
Example 31	Example 8	White	White	322	43.5	7.40	349	51.7	6.75	○	○
Example 32	Example 9	White	White	318	44.6	7.13	473	78.5	6.03	○	○
Example 33	Example 11	White	White	329	44.7	7.36	359	53.1	6.18	○	○
Example 34	Example 12	White	White	177	35.2	5.03	183	38.5	4.75	○	○
Comp. Ex. 23	Comp. Ex. 1	White	White	63	29.7	2.12	Unmeasurable	Unmeasurable	—	×	○
Comp. Ex. 24	Comp. Ex. 2	White	White	68	29.2	2.33	Unmeasurable	Unmeasurable	—	×	○
Comp. Ex. 25	Comp. Ex. 3	White	White	303	45.3	6.69	Unmeasurable	Unmeasurable	—	○	○
Comp. Ex. 26	Comp. Ex. 4	White	White	208	31.9	6.52	Unmeasurable	Unmeasurable	—	△	○
Comp. Ex. 27	Comp. Ex. 5	White	White	277	39.1	7.08	Unmeasurable	Unmeasurable	—	○	○
Comp. Ex. 28	Comp. Ex. 6	White	White	269	38.4	7.01	Unmeasurable	Unmeasurable	—	○	○
Comp. Ex. 29	Comp. Ex. 7	White	White	235	41.0	5.73	Unmeasurable	Unmeasurable	—	○	○
Comp. Ex. 30	Comp. Ex. 9	White	White	315	43.2	7.29	Unmeasurable	Unmeasurable	—	○	○
Comp. Ex. 31	Comp. Ex. 10	White	Yellowish brown	132	36.9	3.58	Unmeasurable	Unmeasurable	—	○	×
Comp. Ex. 32	Comp. Ex. 10	White	White	292	41.2	7.09	705	135.2	5.21	○	×
Comp. Ex. 33	Comp. Ex. 11	Yellow	Yellowish brown	332	47.6	6.97	401	68.5	5.85	○	×

Table 3

	Samples	Curing time (Hrs.)
Example 35	Sample of Ex. 3 120 Parts by weight	2. 0
Example 36	Sample of Ex. 4 120 Parts by weight	2. 5
Example 37	Sample of Ex. 3 80 Parts by weight + Sample of Comp. Ex. 10 40 Parts by weight	3. 5
Example 38	Sample of Ex. 3 60 Parts by weight + Sample of Comp. Ex. 10 60 Parts by weight	5. 5
Example 39	Sample of Ex. 3 40 Parts by weight + Sample of Comp. Ex. 10 80 Parts by weight	7. 5
Example 40	Sample of Ex. 4 80 Parts by weight + Sample of Comp. Ex. 11 40 Parts by weight	4. 0
Example 41	Sample of Ex. 4 60 Parts by weight + Sample of Comp. Ex. 11 60 Parts by weight	6. 0
Example 42	Sample of Ex. 4 40 Parts by weight + Sample of Comp. Ex. 11 80 Parts by weight	8. 0
Comp. Ex. 34	Sample of Comp. Ex. 10 120 Parts by weight	9. 0
Comp. Ex. 35	Sample of Comp. Ex. 11 120 Parts by weight	10. 0

It is apparent from Table 2 that the compositions containing the surface-treated calcium carbonate fillers of the present invention are remarkably superior in storage stability, thixotropy and slump resistance.

It is also apparent from Table 3 that if the surface-treated calcium carbonate fillers of the present invention are used in combination with the conventional surface-treated calcium carbonate filler, the drawback of the conventional filler being long in curing time can be solved and the curing time can be shortened.

Examples 43 to 53, Comparative Examples 36 to 43

The powders obtained by Examples 1 to 9, 11, 12, and Comparative Examples 1 to 7, 9 were used and polyvinyl chloride sheets were prepared by the following blending ratios and the kneading method and the properties were evaluated by the following tests. The results are shown in Table 4.

[Blending ratios]

Polyvinyl chloride resin (S-1001 manufactured by Nippon Vinyl Co., Ltd.)	100 parts by weight
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DOP	50 parts by weight
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Tribase (TS-100 manufactured by Kikuchi Shikiso Co., Ltd.)	
--	--

3 parts by weight

Lead stearate (NS-100 manufactured by Kikuchi Shikiso Co., Ltd.)	
--	--

1 part by weight

Samples: surface-treated calcium carbonate filler	50 parts by weight
---	--------------------

[Method for preparing polyvinyl chloride sheets]

The compositions were kneaded by the use of rolls at 165°C for 6 minutes to take out a sheet of 2-mm thickness. The sheet taken out was inserted between two sheets of iron plates and after being pre-heated by hand press heated to 170°C for 7 minutes, it was pressurized with a pressure of 7.8 MPa (80 Kg/cm²) for 3 minutes. After cooling the iron plates, the sheet was taken out. The thickness of the sheet was 1 mm.

[Volume resistivity test]

Volume resistivity of the sheets obtained was measured according to JIS K 6723.

[Dispersibility test]

The surface of the sheets obtained was observed with naked eyes according to the following criteria:

○ : good

△ : slightly bad

× : bad

Table 4

	Items Samples	Volume resistivity ($\times 10^{-12} \Omega \text{ c m}$)	Dispersibility
Example 43	Example 1	8 0 . 5	○
Example 44	2	7 1 . 2	○
Example 45	3	7 7 . 4	○
Example 46	4	6 5 . 8	○
Example 47	5	7 0 . 6	○
Example 48	6	8 8 . 1	○
Example 49	7	8 2 . 9	○
Example 50	8	6 6 . 2	○
Example 51	9	4 4 . 0	○
Example 52	11	5 2 . 4	○
Example 53	12	6 3 . 1	○
Comp. Ex. 36	1	5 5 . 3	×
Comp. Ex. 37	2	3 1 . 6	×
Comp. Ex. 38	3	4 . 4	○
Comp. Ex. 39	4	4 5 . 3	×
Comp. Ex. 40	5	2 . 9	○
Comp. Ex. 41	6	5 . 1	○
Comp. Ex. 42	7	6 . 2	○
Comp. Ex. 43	9	3 . 3	○

It is apparent from Table 4 that the compositions containing the surface-treated calcium carbonate fillers of the present invention are prominently superior in dispersibility and insulation property.

Example 54, Comparative Example 44

The powders obtained by Example 10 and Comparative Example 8 were kneaded by the use of a sand mill at the following blending ratios and aqueous ink resin compositions were prepared. The properties were evaluated by the following tests. The results are shown in Table 5.

[Blending ratios]

Resin (JOHNCRYL J-69 manufactured by Johnson Polymer Co., Ltd.)	100 parts by weight
Water	18 parts by weight
Silicone anti-foam agent	0.8 part by weight
Colorant (FASTOGEN TGR manufactured by Dainippon Ink & Chemicals, Inc.)	20 parts by weight
Samples: surface-treated calcium carbonate filler	15 parts by weight

[Water resistance test]

Each of the aqueous printing ink compositions was developed on a coated paper Rengo CRC (manufactured by Rengo Co., Ltd.) by the use of a barcoater. The developed paper was rubbed five times with a water-contained cloth under a load of 2.0N (200 g) and evaluation was made by a degree of ink transferred to the cloth.

○ : No ink is transferred to the cloth.

× : Ink is considerably transferred to the cloth.

Table 5

	Item Samples	Water resistance
Example 54	Example 10	○
Comp. Ex. 44	Comp. Ex. 8	×

It is apparent from Table 5 that the ink composition containing the surface-treated calcium carbonate filler of the present invention is superior in water resistance.

Examples 55 to 65, Comparative Examples 45 to 52

The powders obtained by Examples 1 to 9, 11, 12, and Comparative Examples 1 to 7, 9 were dispersed by the use of a sand mill up to the particle size of not larger than $25\mu\text{m}$ and alkyd resin paint compositions were prepared and the properties were evaluated by the following tests. The results are shown in Table 6.

[Blending ratios]

Alkyd resin (BECKOSOL P-470-70 manufactured by Dainippon Ink & Chemicals, Inc.) 250 parts by weight

Titan dioxide (TIPAQUE R-820 manufactured by Ishihara Sangyo Kaisha,

Ltd.)	120 parts by weight
Heavy calcium carbonate (Super SSS manufactured by Maruo Calcium Co., Ltd.)	33 parts by weight
Mineralspirit	70 parts by weight
Dryer	14 parts by weight
Anti-skinning agent (DISPARLON #501 manufactured by Kusumoto Kasei Co., Ltd.)	1.5 parts by weight
Glass beads	350 parts by weight
Samples:surface-treated calcium carbonate filler	58 parts by weight
[Gloss and water resistance test]	

Each of the alkyd resin paint compositions was applied to one surface of a glass plate in the thickness of 4 mils by the use of an applicator, dried at room temperature for 24 hours and gloss at 60 ° was measured by the use of Murakami gloss meter. Thereafter, the glass plate was dipped in water and gloss characteristics after 3 days were evaluated.

Table 6

	Items Samples	Initial gloss 60°	Gloss after water resistance test 60°	Retention of gloss (%)
Example 55	Example 1	87.8	86.1	98.1
Example 56	Example 2	86.9	85.5	98.4
Example 57	Example 3	91.2	90.7	99.5
Example 58	Example 4	92.3	92.2	99.9
Example 59	Example 5	91.7	91.3	99.6
Example 60	Example 6	92.1	91.5	99.3
Example 61	Example 7	91.8	91.2	99.3
Example 62	Example 8	91.1	90.4	99.2
Example 63	Example 9	90.9	89.1	98.0
Example 64	Example 11	90.5	89.8	99.2
Example 65	Example 12	79.8	79.3	99.3
Comp. Ex. 45	Example 1	78.1	65.9	84.4
Comp. Ex. 46	Example 2	76.6	63.5	82.9
Comp. Ex. 47	Example 3	75.4	67.7	89.8
Comp. Ex. 48	Example 4	85.4	78.1	91.5
Comp. Ex. 49	Example 5	86.6	77.5	89.5
Comp. Ex. 50	Example 6	85.4	77.2	90.4
Comp. Ex. 51	Example 7	83.8	72.9	87.0
Comp. Ex. 52	Example 9	74.4	62.9	84.5

It is apparent from Table 6 that the compositions containing the surface-treated calcium carbonate fillers of the present invention are superior in water resistance.

[Total evaluation]

The surface-treated calcium carbonate fillers of Examples 1 to 12 and Comparative Examples 1 to 11 were totally evaluated from the foregoing test results. The results are shown in Table 7.

◎ : Extremely excellent performance is exhibited.

○ : Excellent performance is exhibited.

△ : Performance is not enhanced, though they are usable.

× : Performance is degraded.

Table 7

	Total evaluation
Example 1	○
Example 2	○
Example 3	◎
Example 4	◎
Example 5	◎
Example 6	◎
Example 7	◎
Example 8	◎
Example 9	○
Example 10	◎
Example 11	◎
Example 12	◎
Comp. Ex. 1	×
Comp. Ex. 2	×
Comp. Ex. 3	△
Comp. Ex. 4	×
Comp. Ex. 5	△
Comp. Ex. 6	△
Comp. Ex. 7	△
Comp. Ex. 8	△
Comp. Ex. 9	△
Comp. Ex. 10	△
Comp. Ex. 11	△

Industrial Applicability

As stated above, the surface-treated calcium carbonate fillers of the present invention are suited for fillers for resins in particular, for example, when used in curing type resin compositions, excellent heat resistance upon drying, excellent thixotropy and slump resistance, and good storage stability are exhibited, when used in plastics, excellent dispersibility and insulation property are exhibited, and when used in paints and inks, excellent water resistance is exhibited.



Claims

1. A surface-treated calcium carbonate filler, in which the surface of calcium carbonate is wet-surface-treated with at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids.

2. A surface-treated calcium carbonate filler, in which the surface of calcium carbonate is wet-surface-treated with at least one surface-treating agent selected from the group consisting of metallic soaps of saturated fatty acids, metallic soaps of unsaturated fatty acids, metallic soaps of alicyclic carboxylic acids and metallic soaps of resin acids, and a content of alkali metals is not more than 1.0×10^{-3} mol/100 g CaCO_3 .

3. A surface-treated calcium carbonate filler of Claim 1 or 2, wherein a BET specific surface area of the calcium carbonate is 3 to 120 m^2/g .

4. A method for producing the surface-treated calcium carbonate filler of Claim 1 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, and

heating the resulting mixture to a temperature of not lower than a melting point of these acids to thereby surface-treating the



calcium carbonate.

5. A method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, (A) at least one surface-treating agent selected from the group consisting of saturated fatty acids, unsaturated fatty acids, alicyclic carboxylic acids and resin acids, and (B) a metallic hydroxide or a metallic oxide which is capable of producing a water-insoluble metallic soap through the reaction with (A), and

surface-treating the calcium carbonate with a metallic soap of (A) obtained through the reaction of (A) and (B).

6. A method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, at least one surface-treating agent selected from the group consisting of a metallic soap of saturated fatty acids, a metallic soap of unsaturated fatty acids, a metallic soap of alicyclic carboxylic acids and a metallic soap of resin acids in an organic solvent slurry,

dehydrating and drying the resulting slurry, and

heating the resulting mixture to a temperature of not lower than a melting point of the metallic soap added to thereby surface-treat the calcium carbonate.

7. A method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:



adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids,

surface-treating the calcium carbonate with the surface-treating agent, and

washing the treated calcium carbonate with water to thereby control a content of alkali metals to not more than 1.0×10^{-3} mol/100 g CaCO_3 .

8. A method for producing the surface-treated calcium carbonate filler of Claim 2 or 3 which comprises the steps of:

adding to an aqueous slurry containing calcium carbonate, (C) at least one surface-treating agent selected from the group consisting of alkali metal salts of saturated fatty acids, alkali metal salts of unsaturated fatty acids, alkali metal salts of alicyclic carboxylic acids and alkali metal salts of resin acids,

surface-treating the calcium carbonate with the surface-treating agent,

adding a metallic compound which is capable of producing a metallic soap through the reaction with the alkali metal salts of (C) to thereby conduct double decomposition to a metallic soap of (C), and

washing the treated calcium carbonate with water to thereby control a content of alkali metals to not more than 1.0×10^{-3}



mol/100 g CaCO_3 .

9. A resin composition comprises blending with a resin the surface-treated calcium carbonate filler of any one of Claims 1 to 3.

10. A resin composition of Claim 9, wherein the resin is a resin in use for paints.

11. A resin composition of Claim 9, wherein the resin is a resin in use for inks.

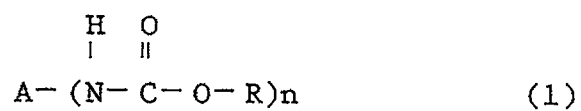
12. A resin composition of Claim 9, wherein the resin is a resin in use for plastics.

13. A resin composition of Claim 9, wherein the resin is a resin in use for sealants.

14. A resin composition of Claim 9, wherein the resin is a curing resin.

15. A resin composition of Claim 9, wherein the resin is a moisture-curing resin.

16. A moisture-curing resin composition comprises blending with a resin the surface-treated calcium carbonate filler of any one of Claims 1 to 3, and (D) calcium carbonate surface-treated with a fatty acid ester and/or a compound having a melting point of not lower than 50°C which is represented by the following formula (1) and at least one selected from the group consisting of carboxylic acids, sulfonic acids, and metal salts thereof:



wherein A is a residual group eliminating an isocyanate group from an isocyanate compound or a residual group eliminating an amino group from an amino compound, n is an integer of 1 to 4, R is a hydrocarbon group in which at least one of R is a hydrocarbon group having carbon atoms of not less than 8.