(54) **SURFACE-TREATED CALCIUM CARBONATE AND RESIN COMPOSITION USING SAME**

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(57) **ABSTRACT**

Surface-treated calcium carbonate of the present invention contains calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent, and satisfies a certain BET specific surface area (Sw), certain loss on heat per unit area (As), a certain lightness maintenance ratio (%), a certain average pore diameter at which an increase in a mercury intrusion amount reaches a maximum value in a certain pore distribution in a mercury intrusion method (Dxp), and a certain average pore diameter amount (maximum value of increase in mercury intrusion amount (Dyp)/ average pore diameter (Dxp)).

SURFACE-TREATED CALCIUM CARBONATE AND RESIN COMPOSITION USING SAME

TECHNICAL FIELD

[0001] The present invention relates to surface-treated calcium carbonate, and a resin composition using the same.

BACKGROUND ART

[0002] Calcium carbonate is often used as an extender pigment for sealants, adhesives, paints, plastisols, and the like. Meanwhile, the prices of organic thickeners and silica are increasing dramatically along with uncertainty of supply of imported materials and an increase in cost of imported materials in recent years. Thus, calcium carbonate, which can be obtained by using Japanese limestone as a raw material, gains increasing attention, and colloidal calcium carbonate that is fine and is highly dispersed is desired for the purpose of imparting high viscosity and thixotropy.

[0003] In addition, regarding, for example, sealing materials and the like to be used for houses, products that have a super long-term assurance effective for a long period of time such as 30 years or 50 years rather than a conventional 10-year assurance have been increasing in number, and thus resin compositions to be used in such products are required to have not only favorable storage stability but also super long-term durability after application and curing. Also, paints and the like to be used for outdoor buildings are required to have higher durability so as to be resistant to high temperatures and solar irradiation during days in summer in recent years on which the maximum temperature exceeds 35° C.

[0004] To meet such needs, for example, Patent Document 1 discloses surface-treated calcium carbonate constituted by fine and highly dispersed colloidal calcium carbonate capable of imparting high viscosity and thixotropy to a resin composition.

[0005] However, although the surface-treated calcium carbonate disclosed in Patent Document 1 is fine and has high dispersibility, a further improvement in thermal stability of the powder is desired. In addition, for a resin composition containing the surface-treated calcium carbonate, it is also desired to improve the storage stability of the resin composition itself and its super long-term durability after application.

RELATED ART DOCUMENTS

Patent Documents

[0006] Patent Document 1: Japanese Patent No. 3650391

SUMMARY OF INVENTION

Problem to be Solved by the Invention

[0007] The present invention was achieved in order to solve the aforementioned problems, and it is an object thereof to provide surface-treated calcium carbonate that has favorable fineness and dispersibility, has excellent thermal stability, and is capable of improving the storage stability of a resin blended therewith and the durability thereof after application, and a resin composition using the surface-treated calcium carbonate.

Means for Solving the Problem

[0008] The present invention is a surface-treated calcium carbonate comprising calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent,

[0009] wherein the fatty acid-based surface treatment agent is at least one compound selected from the group consisting of fatty acids and fatty acid salts, and

[0010] relational expressions (a) to (f) below are satisfied:

[0011] (a) $20 \leq Sw \leq 100$ (m^2/g)

[0012] (b) $1.0 \leq As \leq 7.5$ (mg/m^2)

[0013] (c) $LC \geq 55$ (%)

[0014] (d) $0.003 \leq Dxp \leq 0.03$ (μm)

[0015] (e) $50 \leq Dyp/Dxp \leq 180$

[0016] (f) $0.03 \leq Is \leq 2.57$ $(\mu mol/m^2)$

where

[0017] Sw is a BET specific surface area (m^2/g) that is determined through a nitrogen adsorption method,

[0018] As is loss on heat per unit surface area (mg/m^2) that is determined using the following formula:

$$As = (\text{loss on heat per 1 g of the surface−treated calcium}$$
$$\text{carbonate (mg/g) between 200° C. and 500° C.})/Sw(m^2/g),$$

[0019] LC is a lightness maintenance ratio (%) that is determined using the following formula:

$$LC = (\text{an } L \text{ value of a paste obtained by mixing the surface−treated}$$
$$\text{calcium carbonate heated at 160° C. for 12 hours and diisononyl}$$
$$\text{phthalate at a mass ratio of 1 to 2})/(\text{an } L \text{ value of a paste obtained}$$
$$\text{by mixing the calcium carbonate prior to heating and diisononyl}$$
$$\text{phthalate at a mass ratio of 1 to 2}) \times 100,$$

[0020] Dxp is an average pore diameter (μm) at which an increase in a mercury intrusion amount (cumulative value of increases in pore volume/log (average pore diameter)) reaches a maximum value (Dyp) in a pore distribution within a pore range of 0.001 to 0.1 μm in a mercury intrusion method, Dyp is the maximum value of an increase in the mercury intrusion amount (mL/g),

[0021] Dyp/Dxp is an average pore diameter amount, and

[0022] Is is an alkali metal content per unit specific surface area $(\mu mol/m^2)$ that is calculated using the following formula:

$$Is = (\text{an alkali metal content per 1 g of the surface−treated calcium}$$
$$\text{carbonate } (\mu mol/g))/\{Sw(m^2/g)\}.$$

[0023] In one embodiment, the calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent satisfies formulae (g) and (h) below:

$$0.005 \leq Dxp \leq 0.025(\mu m), \text{ and} \qquad \text{(g)}$$

$$60 \leq Dyp/Dxp \leq 150. \qquad \text{(h)}$$

[0024] The present invention is also a resin composition comprising the above surface-treated calcium carbonate and a resin.

[0025] In one embodiment, the resin is a sealant resin.

[0026] In one embodiment, the resin is an adhesive resin.

[0027] In one embodiment, the resin is a paint resin.

[0028] In one embodiment, the resin is a plastisol resin.

Effects of the Invention

[0029] With the present invention, surface-treated calcium carbonate that is fine, has high dispersibility, and has excellent thermal stability can be efficiently obtained. When blended into a resin composition, the surface-treated calcium carbonate of the present invention can provide high viscosity and thixotropy and can also improve the storage stability. Furthermore, after being applied as, for example, a sealant, the resin composition can exhibit durability and weather resistance for a super long period of time.

DESCRIPTION OF EMBODIMENTS

Surface-Treated Calcium Carbonate

[0030] The surface-treated calcium carbonate of the present invention satisfies the following relational expressions (a), (b), (c), (d), (e), and (f):

$$20 \leq Sw \leq 100 \quad (m^2/g) \qquad \text{(a)}$$

$$1.0 \leq As \leq 7.5 \quad (mg/m^2) \qquad \text{(b)}$$

$$LC \geq 55 \quad (\%) \qquad \text{(c)}$$

$$0.003 \leq Dxp \leq 0.03 \quad (\mu m) \qquad \text{(d)}$$

$$50 \leq Dyp/Dxp \leq 180 \qquad \text{(e)}$$

$$0.03 \leq Is \leq 2.57 \quad (\mu mol/m^2). \qquad \text{(f)}$$

(a) BET Specific Surface Area Determined Through Nitrogen Adsorption Method; Sw

[0031] In the relational expression (a), Sw is the BET specific surface area of surface-treated calcium carbonate determined through a nitrogen adsorption method. Sw is 20 m^2/g to 100 m^2/g, preferably 30 m^2/g to 60 m^2/g, and more preferably 30 m^2/g to 50 m^2/g. If Sw is smaller than 20 m^2/g, it is difficult to obtain a resin composition with high viscosity using the obtained surface-treated calcium carbonate. If Sw exceeds 100 m^2/g, the dispersibility and the temporal dispersion stability of the obtained surface-treated calcium carbonate will decrease. Sw as described above can be measured using a method described later in the section of Examples.

[0032] Sw can be controlled by varying the various conditions for production of the surface-treated calcium carbonate of the present invention. Examples of the conditions under which Sw can be controlled to be within the range above include the concentration of lime milk used in car-

bonation reaction as described later, the temperature employed for the carbonation reaction, the concentration of carbon dioxide used, and the type of additive used in the carbonation reaction, as well as combinations thereof. If these conditions are insufficiently satisfied, it may be difficult to obtain surface-treated calcium carbonate with Sw within the range above.

(b) Loss on Heat Per Unit Surface Area; as

[0033] In the relational expression (b), As is the loss on heat per unit surface area (mg/m^2) and is determined using the following formula.

$$As = (\text{loss on heat per 1 g of the surface-treated}$$
$$\text{calcium carbonate } (mg/g) \text{ between } 200° \text{ C. and } 500° \text{ C.})/Sw$$

[0034] In the present invention, As is 1.0 mg/m^2 to 7.5 mg/m^2, preferably 1.5 mg/m^2 to 5.0 mg/m^2, and more preferably 2.0 mg/m^2 to 4.0 mg/m^2. Note that As corresponds to the amount of a fatty acid-based surface treatment agent per unit surface area of surface-treated calcium carbonate (mg/m^2). Some types of commercially available calcium carbonate satisfy the relational expression (a) above and are constituted by fine primary particles. However, in such calcium carbonate, the primary particles of such calcium carbonate coagulate into secondary particles, and the secondary particles further coagulate into tertiary particles, and accordingly, even an amount of a surface treatment agent that covers the calcium carbonate (loss on heat) that is smaller than 1.0 mg/m^2 is sufficient.

[0035] The surface-treated calcium carbonate of the present invention is fine and is highly dispersed, includes few tertiary particles, and has a high content of secondary particles dispersed. Accordingly, if the amount of a surface treatment agent that covers the calcium carbonate (loss on heat) is smaller than 1.0 mg/m^2, it is difficult to sufficiently cover the surface of the calcium carbonate with the surface treatment agent. Furthermore, if drying and powderization are performed despite insufficient treatment, untreated surfaces will attach to each other, resulting in formation of tertiary particles, and therefore, the effects of imparting high viscosity and high thixotropy, which are the object of the present invention, will not be obtained. On the other hand, if the amount of a surface treatment agent that covers the calcium carbonate (loss on heat) exceeds 7.5 mg/m^2, the storage stability of the surface-treated calcium carbonate will decrease due to an excess of the surface treatment agent, and when the surface-treated calcium carbonate is blended into a resin composition, the surface treatment agent will separate from the resin component and a plasticizer component, which will cause a decrease in physical properties. The loss on heat per unit specific surface area (As) as described above can be determined using a method described later in the section of Examples.

[0036] As can be controlled by varying the various conditions for production of the surface-treated calcium carbonate of the present invention. Examples of the conditions under which As can be controlled to be within the range above include the amount of usage of the surface treatment agent as described later, and the temperature employed for the surface treatment, as well as combinations thereof. If

these conditions are insufficiently satisfied, it may be difficult to obtain surface-treated calcium carbonate with As within the range above.

(c) Lightness Maintenance Ratio; LC

[0037] In the relational expression (c), LC is the lightness (L value) maintenance ratio (%) and is determined using the following formula.

$$
\begin{aligned}
LC = &\left(L \text{ value of paste obtained by mixing} \right. \quad\quad (c1)\\
&\text{surface-treated calcium carbonate heated at } 160° \text{ C. for}\\
&\text{12 hours and diisononyl phthalate at mass ratio of 1 to 2}\Big)/\\
&\left(L \text{ value of paste obtained by mixing surface-treated}\right.\\
&\text{calcium carbonate prior to heating and diisononyl}\\
&\left.\text{-phthalate at mass ratio of 1 to 2}\right) \times 100
\end{aligned}
$$

[0038] In the present invention, LC is 55% or more, preferably 58% or more, and more preferably 60% or more. LC can serve as an index of the thermal resistance of the obtained surface-treated calcium carbonate. If the LC is less than 55%, the obtained surface-treated calcium carbonate powder will have low thermal resistance, leading to variation in the physical properties caused by thermal degradation during drying, and a decrease in the storage stability, in the production process of the surface-treated calcium carbonate. In addition, blending such surface-treated calcium carbonate into a sealant, an adhesive, a paint, or a plastisol will lead to a decrease in the storage stability and deterioration of the thermal resistance and the weather resistance after application.

[0039] The lightness (L value) maintenance ratio (LC) can be measured using a method described later in the section of Examples.

[0040] LC can be controlled by varying the various conditions for production of the surface-treated calcium carbonate of the present invention. Examples of the conditions under which LC can be controlled to be within the range above include the amount of usage of the surface treatment agent as described later, the temperature employed for the surface treatment, and the type and amount of additive used in the carbonation reaction, as well as combinations thereof. If these conditions are insufficiently satisfied, it may be difficult to obtain surface-treated calcium carbonate with LC within the range above.

(d) Average Pore Diameter at Which Increase in Mercury Intrusion Amount Reaches Maximum Value; Dxp

[0041] In the relational expression (d), Dxp is an average pore diameter (μm) at which an increase in the mercury intrusion amount (cumulative value of increases in pore volume/log (average pore diameter)) reaches the maximum value (Dyp) in the pore distribution within a pore range of 0.001 μm to 0.1 μm, the pore range being measured using a mercury intrusion method (porosimeter). Dxp means the fineness of gaps between the surface-treated calcium carbonate particles, and serves as an index of the dispersion state of the surface-treated calcium carbonate.

[0042] In the present invention, Dxp represents the average diameter of gaps between primary particles rather than

the fineness of the particles represented by the BET specific surface area (m^2/g) determined by the nitrogen adsorption method in the relational expression (a) above. Dxp is 0.003 μm to 0.03 μm, preferably 0.005 μm to 0.025 μm, and more preferably 0.006 μm to 0.020 μm. If Dxp is less than 0.003 μm, the obtained surface calcium carbonate may lack temporal stability due to primary particles or secondary particles being too fine. If Dxp exceeds 0.03 μm, it is difficult to obtain a resin composition with high viscosity using the obtained surface-treated calcium carbonate due to primary particles being too large, or many secondary particles being formed through strong coagulation of primary particles.

[0043] Here, "the increase in the mercury intrusion amount" means an increase in the pore volume and is calculated using a formula "(cumulative value of increases in pore volume/log (average pore diameter))", and the unit thereof is mL/g. The smaller the pore diameter is, the smaller the pore volume is, and therefore, the maximum increase in the mercury intrusion amount (Dyp) depends on the average pore diameter (Dxp).

[0044] Dxp can be controlled by varying the various conditions for production of the surface-treated calcium carbonate of the present invention. Examples of the conditions under which Dxp can be controlled to be within the range above include: the concentration of lime milk used in carbonation reaction as described later, the temperature employed for the carbonation reaction, the concentration of carbon dioxide used, and the type of additive used in the carbonation reaction; the concentration of calcium carbonate employed in aging, the aging temperature, and the aging time; and the amount of usage of the surface treatment agent; as well as combinations thereof. If these conditions are insufficiently satisfied, it may be difficult to obtain surface-treated calcium carbonate with Dxp within the range above.

(e) Dyp/Dxp

[0045] In the relational expression (e), Dyp/Dxp represents the number of pores having the average pore diameter in the expression (d), and serves as an index of high viscosity, which is the object of the present invention. As mentioned above, the smaller the pore diameter is, the smaller the pore volume is, and therefore, the number of pores having the average pore diameter can be derived using the maximum increase in mercury intrusion amount (Dyp), and the average pore diameter (Dxp) obtained from the relational expression (d). The larger the numerical value of Dyp/Dxp is, the higher the viscosity of a resin composition blended with the obtained surface-treated calcium carbonate. Dyp/Dxp also serves as an index of the dispersion state of the surface-treated calcium carbonate.

[0046] In the present invention, Dyp/Dxp is 50 to 180, preferably 60 to 150, and more preferably 70 to 130. If Dyp/Dxp is smaller than 50, it is difficult to obtain a resin composition with high viscosity using the obtained surface-treated calcium carbonate. If the Dyp/Dxp exceeds 180, primary particles or secondary particles may lack temporal stability due to the average pore diameter being excessively small.

[0047] Note that, if the obtained surface-treated calcium carbonate is out of the range of the relational expression (d) or (e) above, for example, a paint composition blended with such calcium carbonate may have low thixotropy, and a sealant composition blended with such calcium carbonate may have decreased strength.

[0048] The mercury intrusion (porosimeter) measurement used to determine whether or not the ranges of the relational expressions (d) and (e) are satisfied can be performed according to a method described later in the section of Examples.

[0049] Dyp/Dxp can be controlled by varying the various conditions for production of the surface-treated calcium carbonate of the present invention. Examples of the conditions under which Dyp/Dxp can be controlled to be within the range above include the concentration of calcium carbonate employed for aging as described later, the aging temperature, and the aging time, as well as combinations thereof. If these conditions are insufficiently satisfied, it may be difficult to obtain surface-treated calcium carbonate with Dyp/Dxp within the range above.

(f) Alkali Metal Content per Unit Specific Surface Area; Is

[0050] In the relational expression (f), Is is the alkali metal content per unit specific surface area ($\mu mol/m^2$) calculated using the formula (f1) below.

$$Is = \left(\text{alkali metal content per 1 g of surface−treated calcium} \qquad \text{(f1)}\right.$$
$$\left. \text{carbonate } (\mu mol/g)\right)/\left\{Sw(m^2/g)\right\}$$

[0051] In the present invention, Is is 0.03 $\mu mol/m^2$ to 2.57 $\mu mol/m^2$, preferably 0.15 $\mu mol/m^2$ to 2.2 $\mu mol/m^2$, and more preferably 0.3 $\mu mol/m^2$ to 2.0 $\mu mol/m^2$. If Is is less than 0.03 $\mu mol/m^2$, the surface treatment state of the obtained surface-treated calcium carbonate tends to be poor. Accordingly, when the surface-treated calcium carbonate is blended into a resin composition, sufficiently high viscosity is not imparted in some cases due to a decrease in the dispersibility of the surface-treated calcium carbonate. Meanwhile, among alkali metal compounds, for example, sodium compounds are known to have high exothermic reactivity and easily react with moisture outside the system. Therefore, if the obtained surface-treated calcium carbonate contains a sodium compound as an alkali metal compound and Is exceeds 2.57 mol/m^2 in this case, the storage stability of, for example, a sealing material in which the surface-treated calcium carbonate is used may decrease.

[0052] Here, the "alkali metal content per 1 g of surface-treated calcium carbonate ($\mu mol/g$)" used to calculate Is using the formula (f1) above can be measured using, for example, a method described later in the section of Examples.

[0053] Is can be controlled by monitoring, as appropriate, the alkali metal content in raw materials, a surface treatment agent, and/or additives used to produce the surface-treated calcium carbonate of the present invention and adjusting the amount of usage thereof. Is can be controlled by, for example, adjusting the amount of usage of the surface treatment agent in accordance with the specific surface area of calcium carbonate before surface treatment. If this amount of usage is insufficiently adjusted, it may be difficult to obtain surface-treated calcium carbonate with Is within the range above.

[0054] Calcium Carbonate Subjected to Surface Treatment with Fatty Acid-Based Surface Treatment Agent

[0055] The surface-treated calcium carbonate of the present invention that satisfies the relational expressions (a), (b),

(c), (d), (e), and (f) above is constituted by calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent, which is one type of organic acid-based surface treatment agents. That is to say, the surface-treated calcium of the present invention is in the form of a composition containing calcium carbonate as a main component.

[0056] A production method for the surface-treated calcium carbonate of the present invention is not particularly limited as long as the surface-treated calcium carbonate is fine and has high dispersibility and excellent thermal resistance.

[0057] The following is a specific description of an example of a preferable production method for the surface-treated calcium carbonate of the present invention.

(1) Carbonation Reaction

[0058] First, calcium carbonate before surface treatment can be obtained by adding additives (e.g., a complex-forming agent for promoting formation of a complex with a calcium component, and an inorganic acid and/or a salt thereof) to lime milk, introducing carbon dioxide to the lime milk, performing carbonation reaction to produce a calcium carbonate slurry, and then aging the slurry, for example, according to a conventional method as described in JP H10-72215A, but there is no particular limitation to this procedure.

[0059] Examples of the complex-forming agent include: hydroxycarboxylic acids such as citric acid, oxalic acid, and malic acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof, polyhydroxycarboxylic acids such as gluconic acid and tartaric acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof, aminopolycarbons such as imino-diacetic acid, ethylenediaminetetraacetic acid, and nitrilotri-acetic acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof; polyacetic acids such as hexametaphosphoric acid and tripolyphosphoric acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof, and ketones such as acetylacetone, methyl acetoacetate, and allyl acetoacetate; as well as combinations thereof, but are not particularly limited thereto.

[0060] Examples of the inorganic acid and/or a salt thereof include: mineral acids such as sulfuric acid (e.g., concentrated sulfuric acid), hydrochloric acid (e.g., concentrated hydrochloric acid), nitric acid (e.g., concentrated nitric acid), phosphoric acid, boric acid, and hydrofluoric acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof, as well as combinations thereof, but are not particularly limited thereto. It is preferable to use: sulfuric acid (e.g., concentrated sulfuric acid), nitric acid (e.g., concentrated nitric acid), phosphoric acid, alkali metal salts thereof, alkaline earth metal salts thereof, and ammonium salts thereof, as well as combinations thereof, because safety against toxicity, irritant odor, and the like can be ensured, and these substances can be easily used for industrial purposes.

(1-1) Conditions of Carbonation Reaction

[0061] It is preferable to prepare lime milk used in the carbonation reaction such that the concentration thereof is

3.5 mass % to 10.2 mass %. Note that the concentration of lime milk can be varied depending on the type of additive used together.

[0062] For example, when a complex-forming agent is used as an additive, it is more preferable to prepare the lime milk such that the concentration thereof is 6.0 mass % to 8.0 mass %. When an inorganic acid and/or a salt thereof is used as an additive, it is preferable to prepare the lime milk such that the concentration thereof is 4.0 mass % to 7.0 mass %, and more preferably 4.0 mass % to 6.0 mass %. When an inorganic acid and a salt thereof are used together, dispersed calcium carbonate can be obtained immediately after the start of the carbonation reaction. Accordingly, there is an advantage in that time required for aging, which will be described later, can be shortened, and undesired particle growth can be suppressed.

[0063] If the concentration of lime milk used in the carbonation reaction is less than 3.5 mass %, it is not possible to expect that calcium carbonate with further improved dispersibility is obtained, and the cost may increase contrarily. If the concentration of lime milk used in the carbonation reaction exceeds 10.2 mass %, primary particles are likely to coagulate after the carbonation reaction, and thus it may be difficult to obtain calcium carbonate with improved dispersibility despite of aging.

[0064] The addition amount of the additive may be selected as appropriate by a person skilled in the art depending on the type of additive used.

[0065] For example, when a complex-forming agent is used as an additive, the amount of the complex-forming agent added to the lime milk as an additive preferably corresponds to 0.5 mass % to 2.0 mass % based on the total amount of a reaction product after the addition of the complex-forming agent to the lime milk. Here, if the addition amount of the complex-forming agent used as an additive is less than 0.5 mass %, it may be difficult to obtain surface-treated calcium carbonate that is fine and is highly dispersed. If the addition amount of the complex-forming agent used as an additive exceeds 2.0 mass %, the obtained surface-treated calcium carbonate may have insufficient thermal resistance.

[0066] When an inorganic acid and/or a salt thereof is used as an additive, the amount of the inorganic acid and/or the salt thereof added to the lime milk as an additive preferably corresponds to 0.3 mass % to 9.0 mass % based on the total amount of a reaction product after the addition of the inorganic acid and/or the salt thereof to the lime milk. Here, if the addition amount of the inorganic acid and/or the salt thereof used as an additive is less than 0.3 mass %, it may be difficult to obtain surface-treated calcium carbonate that is fine and is highly dispersed. If the addition amount of the inorganic acid and/or the salt thereof used as an additive exceeds 9.0 mass %, there is very little change in the fineness of the obtained surface-treated calcium carbonate, and the productivity may decrease contrarily.

[0067] A temperature that can be employed for the carbonation reaction is, for example, 5° C. to 30° C. For example, when an inorganic acid and/or a salt thereof is used as an additive, the temperature is preferably 5° C. to 20° C., more preferably 5° C. to 15° C., and even more preferably 5° C. to 12° C. for the reason that the BET specific surface area immediately after the carbonation can be increased,

even finer calcium carbonate is thus obtained, and a subsequent aging process for dispersion can be performed more efficiently.

[0068] Carbon dioxide that can be employed for the carbonation reaction may be mixed with air, and it is preferable that the concentration of carbon dioxide is set to 10 vol % to 50 vol % with respect to the total amount of mixed gas of carbon dioxide and air. If the concentration of carbon dioxide is less than 10 vol %, primary particles of calcium carbonate obtained after the reaction may grow to an undesired size. If the concentration of carbon dioxide exceeds 50 vol %, the cost may increase from the industrial viewpoint, and the productivity may decrease. Furthermore, the flow rate of carbon dioxide that can be employed for the carbonation reaction is, for example, 300 L/hour to 3000 L/hour per 1 kg of calcium hydroxide in terms of the flow rate of the mixed gas of carbon dioxide and air. If the flow rate is less than 300 L/hour, primary particles of calcium carbonate obtained after the reaction may grow to an undesired size. If the flow rate exceeds 3000 L/hour, the cost may increase from the industrial viewpoint, and the productivity may decrease.

(1-2) Conditions of Aging

[0069] Calcium carbonate is prepared such that the concentration thereof that can be employed for aging is preferably 2.4 mass % to 13.0 mass %, more preferably 4.0 mass % to 11.0 mass %, and even more preferably 5.0 mass % to 9.0 mass %, based on the total amount of the calcium carbonate slurry irrespective of the type of additive used. If the concentration of calcium carbonate is less than 2.4 mass %, the productivity may decrease from the industrial viewpoint. If the concentration of calcium carbonate exceeds 13.0 mass %, it may be difficult to uniformly stir the system in the case where the structural viscosity in the system increases as a result of an improvement in the dispersibility through aging. The concentration of calcium carbonate employed for aging is important to an improvement in the dispersibility of the obtained surface-treated calcium carbonate. For example, when minute particles of calcium carbonate are used, it is preferable to employ a concentration that is as low as possible within the concentration range above in order to improve the dispersibility.

[0070] A temperature that can be employed for the aging is, for example, 30° C. to 70° C. For example, when an inorganic acid and/or a salt thereof is used as an additive, the temperature is preferably 25° C. to 45° C., more preferably 25° C. to 40° C., and even more preferably 25° C. to 35° C. for the reason that high-temperature aging promotes the growth of particles, and the aging effect is insufficiently exhibited at an excessively low temperature.

[0071] Time that can be employed for the aging can be time required to satisfy the ranges of the relational expressions (d) and (e) above serving as the indices of the dispersibility. When blended into a resin composition, the thus obtained surface-treated calcium carbonate can provide high viscosity. The time for the aging is not particularly limited because it can be varied depending on the conditions above, but it is preferably 24 hours to 120 hours. For example, when an inorganic acid and/or a salt thereof is used as an additive, it can be more preferable to select 30 hours to 100 hours, and it can be even more preferable to select 30 hours to 50 hours, in order to suppress excessive growth of calcium carbonate particles caused by the aging. If the time

for the aging is shorter than 24 hours, it may be difficult to obtain surface-treated calcium carbonate with favorable dispersibility. If the time for the aging exceeds 120 hours, the cost may increase from the industrial viewpoint.

(2) Surface Treatment

[0072] Subsequently, the calcium carbonate is subjected to surface treatment with a fatty acid-based surface treatment agent.

[0073] The fatty acid-based surface treatment agent is not particularly limited as long as a fatty acid and/or a fatty acid salt that can be used for surface treatment of calcium carbonate particles in the art is used, and various fatty acid-based surface treatment agents can be used.

[0074] The fatty acid-based surface treatment agent is, for example, a higher fatty acid, preferably a C6 to C31 fatty acid (i.e., a fatty acid with 6 to 31 carbon atoms), and more preferably a C9 to C21 fatty acid (i.e., a fatty acid with 9 to 21 carbon atoms). Alternatively, the fatty acid-based surface treatment agent may be, for example, a modified or unmodified fatty acid derived from an animal or plant.

[0075] Examples of a fatty acid contained in such a fatty acid-based surface treatment agent include fatty acids such as saturated fatty acids, unsaturated fatty acids, and mixtures of saturated fatty acids and unsaturated fatty acids (e.g., caproic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, 2-ethylbutyric acid, 2-ethylhexanoic acid, isononanoic acid, isodecanoic acid, neodecanoic acid, isotridecanoic acid, isopalmitic acid, isostearic acid, myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, beef tallow stearic acid, palm kernel fatty acids, coconut fatty acids, palm fatty acids, palm stearic acid, beef tallow fatty acids, soybean fatty acids, partially hydrogenated palm kernel fatty acids, partially hydrogenated coconut fatty acids, partially hydrogenated beef tallow fatty acids, partially hydrogenated soybean fatty acids, fully hydrogenated palm kernel fatty acids, fully hydrogenated coconut fatty acids, fully hydrogenated beef tallow fatty acids, and fully hydrogenated soybean fatty acids), as well as combinations thereof and salts thereof. Examples of the fatty acid salt contained in the fatty acid-based surface treatment agent include alkaline metal salts of the fatty acids above (e.g., sodium salts and potassium salts), alkaline earth metal salts of the fatty acids above (e.g., calcium salts and magnesium salts), ammonium salts of the fatty acids above, and amine salts of the fatty acids above, as well as combinations thereof. From the viewpoint of cost and supply stability, it is preferable to use, as the fatty acid-based surface treatment agent, saturated fatty acids and unsaturated fatty acids (e.g., lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, beef tallow stearic acid, palm kernel fatty acids, partially hydrogenated palm fatty acids, fully hydrogenated palm fatty acids, coconut fatty acids, partially hydrogenated coconut fatty acids, fully hydrogenated coconut fatty acids, palm fatty acids, palm stearic acid, beef tallow fatty acids, partially hydrogenated beef tallow fatty acids, fully hydrogenated beef tallow fatty acids, soybean fatty acids, partially hydrogenated soybean fatty acids, and fully hydrogenated soybean fatty acids), as well as combinations thereof and salts thereof.

[0076] Note that, in the present invention, other surface treatment agents may be used together with the above-mentioned fatty acid-based surface treatment agent as long

as the obtained surface-treated calcium carbonate satisfies the ranges of the relational expressions (a) to (f) above. Examples of the other surface treatment agents include sulfonic acids such as alkylbenzenesulfonic acids and salts thereof, fatty acid esters such as stearyl stearate, resin acids such as abietic acid and salts thereof, and metal soaps such as calcium soaps, as well as combinations thereof.

[0077] The surface treatment level (the amount of usage of the fatty acid-based surface treatment agent) depends on the specific surface area of the calcium carbonate dough, and thus is not particularly limited as long as the range of the relational expression (b) above is satisfied. However, the surface treatment level is preferably 3.5 mass % to 50 mass %, more preferably 5 mass % to 40 mass %, and even more preferably 7 mass % to 30 mass %, based on the total amount of the calcium carbonate solid in the calcium carbonate slurry before the treatment. If the surface treatment level is less than 3.5 mass %, it may be difficult to obtain surface-treated calcium carbonate that is fine and has high dispersibility. In addition, if drying and powderization are performed despite such a surface treatment level, the obtained surface-treated calcium carbonate is likely to coagulate via untreated surfaces. Accordingly, when blended into a resin composition, the obtained surface-treated calcium carbonate may have difficulty in providing high viscosity and high thixotropy. If the surface treatment level exceeds 30 mass %, the storage stability of the obtained surface-treated calcium carbonate will decrease due to an excess of the surface treatment agent, and when the surface-treated calcium carbonate is blended into a resin composition, the treatment agent will separate from the surface-treated calcium carbonate and get mixed in the resin component and a plasticizer component, which will cause a decrease in physical properties.

[0078] Although the surface treatment method is not particularly limited, it is preferable to perform the surface treatment under wet conditions in order to improve the surface treatment state. When the surface treatment is performed in an aqueous slurry, it is preferable to perform the surface treatment at a temperature higher than the melting points of the fatty acid and the fatty acid salt used as the surface treatment agent, and the surface treatment temperature in such a case is preferably 20° C. to 98° C., more preferably 40° C. to 90° C., and even more preferably 60° C. to 80° C. If the surface treatment temperature is lower than 20° C., adsorption-binding of the fatty acid-based surface treatment agent to calcium carbonate, which will be described later, is unlikely to occur, which may result in ununiform surface treatment. If the treatment temperature exceeds 98° C., there is a risk of bumping, and a pressure-resistant apparatus may be required separately.

[0079] After the fatty acid-based surface treatment agent is added to calcium carbonate, it is preferable to stir the mixture for a predetermined period of time for the purpose of more uniform surface treatment.

[0080] In one embodiment, the stirring time is, for example, 30 minutes to 24 hours. Here, for example, when a complex-forming agent is used as an additive, the stirring time is preferably set to 6 hours to 24 hours, and more preferably 12 hours to 24 hours, in order to prevent or suppress impairment of the thermal resistance of the obtained surface-treated calcium carbonate due to the com-

plex-forming agent inhibiting adsorption or binding of the fatty acid-based surface treatment agent to calcium carbonate.

[0081] Alternatively, the stirring time may be selected as appropriate by a person skilled in the art depending on the type of additive used. For example, when a complex-forming agent is used as an additive, it can be preferable to select 6 hours to 24 hours, and it can be more preferable to select 12 hours to 24 hours. When the stirring time is shorter than 6 hours, favorable surface treatment state will not be obtained due to an effect of the complex-forming agent to inhibit the adsorption-binding of the fatty acid-based surface treatment agent to calcium carbonate, which may result in ununiform surface treatment and insufficient thermal resistance of the obtained surface-treated calcium carbonate. If the stirring time exceeds 24 hours, it will take long time to produce the surface-treated calcium carbonate, which may result in a decrease in the production efficiency and an increase in the cost.

[0082] After the above-mentioned surface treatment, the obtained particles may be powderized through any operations such as dehydration, drying, and pulverization, for example, according to ordinary methods.

[0083] In this manner, surface-treated calcium carbonate that contains calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent and satisfies the relational expressions (a) to (f) above can be obtained.

Resin Composition

[0084] The above-mentioned surface-treated calcium carbonate is useful as a constituent material for resin compositions such as a sealing material, an adhesive, a paint, and a plastisol.

[0085] The sealing material contains the surface-treated calcium carbonate of the present invention and a sealant resin. Examples of the sealant resin include a polyurethane resin, a polysulfide resin, a silicone resin, a modified silicone resin, a polyisobutylene resin, an epoxy resin, and a polyester resin as well as combinations thereof, but are not particularly limited thereto.

[0086] In the present invention, the blend ratio between the surface-treated calcium carbonate and the sealant resin is not particularly limited, and can be determined by a person skilled in the art as appropriate in accordance with desired physical properties. In one embodiment, the content of the surface-treated calcium carbonate of the present invention is 1 part by mass to 100 parts by mass with respect to 100 parts by mass of the sealant resin contained in the sealant. Various additives such as a colorant and a stabilizer may be added to the sealant if necessary.

[0087] The adhesive contains the surface-treated calcium carbonate of the present invention and an adhesive resin. Examples of the adhesive resin include a urea resin, a phenol resin, an epoxy resin, a silicone resin, an acrylic resin, a polyurethane resin, and a polyester resin, as well as combinations thereof, but are not particularly limited thereto.

[0088] In the present invention, the blend ratio between the surface-treated calcium carbonate and the adhesive resin is not particularly limited, and can be determined by a person skilled in the art as appropriate in accordance with desired physical properties. In one embodiment, the content of the surface-treated calcium carbonate of the present invention is 1 part by mass to 100 parts by mass with respect

to 100 parts by mass of the adhesive resin contained in the adhesive. Various additives such as a stabilizer and a plasticizer may be added to the adhesive if necessary.

[0089] The paint contains the surface-treated calcium carbonate of the present invention and a paint resin. Examples of the paint resin include: resins for a solvent-based paint such as an alkyd resin, an acrylic resin, a vinyl acetate resin, a urethane resin, a silicone resin, a fluororesin, a styrene resin, a melamine resin, and an epoxy resin; emulsion resins for a general paint such as an alkyd resin, an acrylic resin, a latex resin, a vinyl acetate resin, a urethane resin, a silicone resin, a fluororesin, a styrene resin, a melamine resin, and an epoxy resin; water-soluble resins for a general paint typified by an alkyd resin, an amine resin, a styrene-allyl alcohol resin, an aminoalkyd resin, a polybutadiene resin, and the like; dispersion resins for a paint obtained by blending an emulsion resin for a general paint and a water-soluble resin for a general paint; dispersion resins containing a cross-linked water-soluble resin as an emulsifier; and acrylic hydrosol; as well as combinations thereof, but are not particularly limited thereto.

[0090] In the present invention, the blend ratio between the surface-treated calcium carbonate of the present invention and the paint resin is not particularly limited, and can be determined by a person skilled in the art as appropriate in accordance with desired physical properties. In one embodiment, the content of the surface-treated calcium carbonate of the present invention is 1 part by mass to 100 parts by mass with respect to 100 parts by mass of the paint resin contained in the paint. Various additives such as a plasticizer and a dispersant may be added to the paint if necessary.

[0091] The plastisol contains the surface-treated calcium carbonate of the present invention and a plastisol resin. Examples of the plastisol resin include a vinyl chloride sol, an acrylic sol, a water-soluble acrylic sol, and a urethane sol, as well as combinations thereof, but are not particularly limited thereto.

[0092] In the present invention, the blend ratio between the surface-treated calcium carbonate and the plastisol resin is not particularly limited, and can be determined by a person skilled in the art as appropriate in accordance with desired physical properties. In one embodiment, the content of the surface-treated calcium carbonate of the present invention is 1 part by mass to 100 parts by mass with respect to 100 parts by mass of the plastisol resin contained in the plastisol. Various additives such as a stabilizer may be added to the plastisol if necessary.

[0093] In addition to the above-mentioned surface-treated calcium carbonate and the various resins, fillers such as colloidal calcium carbonate, heavy calcium carbonate, colloidal silica, talc, kaolin, zeolite, a resin balloon, and a glass balloon; plasticizers such as dioctyl phthalate and dibutyl phthalate; petroleum-based solvents such as toluene and xylene; solvents such as ketones (e.g., acetone and methyl ethyl ketone) and ether esters (e.g., cellosolve acetate); silicone oils, fatty acid ester-modified silicone oils; various additives; and colorants; as well as combinations thereof may be contained in the resin composition of the present invention as other components in order to adjust physical properties such as viscosity. The contents of the other components in the resin composition of the present invention are not particularly limited, and a person skilled in the art can select, as appropriate, suitable contents thereof

within such ranges that the effects exhibited by the above-mentioned surface-treated calcium carbonate and various resins are not impaired.

[0094] When the resin composition of the present invention is a curable resin composition such as a sealant or an adhesive, a cured product having excellent viscosity, thixotropy, and storage stability, as well as high thermal stability can be provided. Also, when the resin composition of the present invention is, for example, a paint, even a small amount of the paint has excellent viscosity, thixotropy, anti-sagging properties, and storage stability. In addition, when the resin composition of the present invention is, for example, a resin composition for a plastisol, the resin composition has excellent viscosity and thixotropy, is capable of achieving a weight reduction due to a small amount of the resin composition being blended, and has high storage stability. Also, the thermal stability during baking and curing and after curing are excellent.

EXAMPLES

[0095] Hereinafter, the present invention will be described in detail by way of examples, but the present invention is not limited to these examples. Note that, in the following descriptions, "%" means "mass %" and "part" means "part by mass" unless otherwise stated.

[0096] Measurement apparatuses used in examples and comparative examples were as follows.

(A) BET Specific Surface Area Determined through Nitrogen Adsorption Method (Sw)

[0097] A measurement glass cell filled with 200 mg of the surface-treated calcium carbonate sample obtained in each of the examples and the comparative examples was set in a BET specific surface area analyzer (Macsorb HM Model-1201, manufactured by Mountech Co., Ltd.). After the sample was pretreated at 200° C. for 10 minutes with nitrogen being introduced, and was then cooled for 4 minutes, the BET specific surface area was measured using a one-time measurement method.

[0098] (B) Loss on Heat per Unit Specific Surface Area (As)

[0099] A cylindrical sample pan (made of platinum) with a diameter of 5 mm and a depth of 5 mm filled with 20 mg of surface-treated calcium carbonate was set in a thermal analyzer (ThermoPlusEVO2, manufactured by Rigaku Corporation). The sample was heated from normal temperature to 510° C. at a heating rate of 15° C./minute, and the loss on heat between 200° C. and 500° C. was measured. Then, the "loss-on-heat ratio (mg/g) per 1 g of surface-treated calcium carbonate" was calculated. The loss on heat per unit specific surface area was calculated by dividing the loss-on-heat ratio by the BET specific surface area value (Sw).

(C) Lightness (L value) Maintenance Ratio (LC)

[0100] 50 g of the obtained surface-treated calcium carbonate was filled into a crucible (made of a ceramic) and was heated in an electric furnace at 160° C. for 12 hours. 10 g of the surface-treated calcium carbonate before or after the heating and 20 g of diisononyl phthalate (DINP) were filled into a 100-mL PP (polypropylene) cup, and a planetary defoaming kneader (KK-1000W, manufactured by Kurabo Industries Ltd.) was used to subject the sample to defoaming under a kneading condition of 5-5-6. The powder on the cup wall surface was scraped off, and was then subjected to defoaming under a kneading condition of May 5, 2018. Thus, a paste was produced. Here, in the kneading condition

"a-b-c" above, "a" represents a revolution condition, "b" represents a rotation condition, and "c" represents time (c×10 seconds).

[0101] Next, the paste obtained as described above was filled into a reflection measurement cell (with a diameter of 3 mm) for a color-difference meter (Color meter ZE 6000, manufactured by Nippon Denshoku Industries Co., Ltd.) to about 80% of the cell volume. The color differences, L, a, and b values, were measured through the reflection measurement, and the L value obtained through the color difference measurement was employed as the lightness. Then, the lightness maintenance ratio was calculated as a percentage (%) according to the formula (c1) below.

$$LC = (L \text{ value of paste obtained by mixing} \qquad (c1)$$
$$\text{surface–treated calcium carbonate heated at } 160° \text{ C. for}$$
$$12 \text{ hours and diisononyl phthalate at mass ratio of } 1 \text{ to } 2)/$$
$$(L \text{ value of paste obtained by mixing surface–treated}$$
$$\text{calcium carbonate prior to heating and diisononyl}$$
$$\text{–phthalate at mass ratio of } 1 \text{ to } 2) \times 100$$

(D) Average Pore Diameter at Which Increase in Mercury Intrusion Amount Reaches Maximum Value (Dxp)

[0102] About 0.10 g of the surface-treated calcium carbonate was filled into a measurement cell (with a cell constant of 10.79 ml/pF), and the average pore diameter (Dxp) at which an increase in the mercury intrusion amount reached the maximum value was measured using a mercury porosimeter pore distribution measurement apparatus (Auto-Pore IV, manufactured by Shimadzu Corporation). Here, the measurement conditions employed in this measurement were as follows: mercury was of 99.99% purity, the surface tension was 480 dyns/cm, and the contact angle was 135°.

(E) Dyp/Dxp

[0103] Dyp/Dxp was calculated using the maximum value of an increase in the mercury intrusion amount (Dyp) measured in (D) above and the average pore diameter (μm) (Dxp).

(F) Alkali Metal Content per Unit Specific Surface Area (Is)

[0104] First, 0.5 g of the surface-treated calcium carbonate obtained in each of the examples and the comparative examples was filled into a crucible (made of a ceramic) and was fired in an electric furnace at 300° C. for 3 hours. Subsequently, the sample was allowed to cool and was placed in a 200-mL beaker. 60 mL of distilled water and 7.5 mL of 61% nitric acid were added to the sample in this order, and the top of the beaker was covered with a watch glass. Then, the mixture was boiled using an electrothermal heater to completely dissolve the calcium carbonate. After cooled at normal temperature, the mixture was diluted to 100 mL using a volumetric flask and filtered. Thus, a measurement sample was produced.

[0105] Subsequently, this measurement sample was used to measure the alkali metal content (μmol/g) per 1 g of the surface-treated calcium carbonate with an atomic absorption measurement apparatus (polarized Zeeman atomic absorp-

tion spectrophotometer ZE3300, manufactured by Hitachi High-Tech Corporation). Then, the alkali metal content per unit specific surface area (μmol/m^2) was calculated according to the formula (f1) below using the alkali metal content (μmol/g) and the BET specific surface area (Sw) obtained above.

$$Is = \left(\text{alkali metal content per 1 g of} \right. \tag{f1}$$

$$\text{surface-treated calcium carbonate } (\mu\text{mol/g})\right)/\left\{Sw(\text{m}^2/\text{g})\right\}$$

Example 1: Production of Surface-Treated Calcium Carbonate (E1)

[0106] Concentrated sulfuric acid was added to lime milk with a concentration of 5% at a temperature of 10° C. such that the amount thereof was 4.5% with respect to the mass of calcium hydroxide contained in the lime milk. Then, into the resulting mixture, mixed gas of CO_2 and air containing 20 vol % of CO_2 gas was introduced at a rate of 1700 L/hour per 1 kg of calcium hydroxide to produce a calcium carbonate slurry with a concentration of 6.8%. Subsequently, the calcium carbonate slurry was aged through stirring at a temperature of 30° C. to 35° C. for 30 hours. Then, a 10% aqueous solution of sodium beef tallow fatty acid (fatty acid-based surface treatment agent) (FA-T manufactured by Miyoshi Oil&Fat Co., Ltd., sodium-neutralized) obtained through thermal dissolution of the sodium beef tallow fatty acid in warm water was added to the calcium carbonate slurry such that the sodium beef tallow fatty acid solid was 14% of the calcium carbonate solid. The resulting mixture was stirred for 2 hours, and was then subjected to dehydration, drying, and powderization. Thus, calcium carbonate (E1) that had been subjected to surface treatment with the fatty acid-based surface treatment agent and had a BET specific surface area (Sw) of 45 m^2/g was obtained. The physical property values of the obtained surface-treated calcium carbonate (E1) are shown in Table 1.

Example 2: Production of Surface-Treated Calcium Carbonate (E2)

[0107] Calcium carbonate (E2) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was produced in the same manner as in Example 1, except that the addition amount of the concentrated sulfuric acid was changed to 3.0% and the addition amount of the sodium beef tallow fatty acid was changed to 12%. The physical property values of the obtained surface-treated calcium carbonate (E2) are shown in Table 1.

Example 3: Production of Surface-Treated Calcium Carbonate (E3)

[0108] Citric acid serving as a complex forming agent was added to lime milk with a concentration of 5% at a temperature of 10° C. such that the amount thereof was 2.0% with respect to the mass of calcium hydroxide. Then, into the resulting mixture, mixed gas of CO_2 and air containing 20 vol % of CO_2 gas was introduced at a flow rate of 1700 L/hour per 1 kg of calcium hydroxide to produce a calcium carbonate slurry with a concentration of 9.5%. Subsequently, the calcium carbonate slurry was aged through stirring at a temperature of 45° C. to 50° C. for 50 hours.

Then, a 10% aqueous solution of sodium beef tallow fatty acid (fatty acid-based surface treatment agent) obtained through thermal dissolution of the sodium beef tallow fatty acid in warm water was added to the calcium carbonate slurry such that the sodium beef tallow fatty acid solid was 13% of the calcium carbonate solid. The resulting mixture was stirred for 24 hours to allow the surface treatment agent to sufficiently adsorb on the surface of the calcium carbonate, and was then subjected to dehydration, drying, and powderization. Thus, calcium carbonate (E3) that had been subjected to surface treatment with the fatty acid-based surface treatment agent and had a BET specific surface area (Sw) of 42 m^2/g was obtained. The physical property values of the obtained surface-treated calcium carbonate (E3) are shown in Table 1.

Example 4: Production of Surface-Treated Calcium Carbonate (E4)

[0109] Surface-treated calcium carbonate (E5) was produced in the same manner as in Example 1, except that Sodium Palm Fatty Acid (IPMD manufactured by Miyoshi Oil&Fat Co., Ltd., sodium-saponified) was used as a fatty acid-based surface treatment agent instead of the sodium beef tallow fatty acid. The physical property values of the obtained surface-treated calcium carbonate (E4) are shown in Table 1.

Example 5: Production of Surface-Treated Calcium Carbonate (E5)

[0110] Surface-treated calcium carbonate (E5) was produced in the same manner as in Example 1, except that sodium oleate was used as a fatty acid-based surface treatment agent instead of the sodium beef tallow fatty acid. The physical property values of the obtained surface-treated calcium carbonate (E5) are shown in Table 1.

Comparative Example 1: Production of Surface-Treated Calcium Carbonate (C1)

[0111] Citric acid serving as a complex forming agent was added to lime milk with a concentration of 8% at a temperature of 10° C. such that the amount thereof was 3.0% with respect to the mass of calcium hydroxide. Then, into the resulting mixture, mixed gas of CO_2 and air containing 20 vol % of CO_2 gas was introduced at a flow rate of 1700 L/hour per 1 kg of calcium hydroxide to produce a calcium carbonate slurry with a concentration of 10.8%. Subsequently, the calcium carbonate slurry was aged through stirring at a temperature of 45° C. to 50° C. for 50 hours. Then, a 10% aqueous solution of sodium beef tallow fatty acid (fatty acid-based surface treatment agent) obtained through thermal dissolution of the sodium beef tallow fatty acid in warm water was added to the calcium carbonate slurry such that the sodium beef tallow fatty acid solid was 13% of the calcium carbonate solid. The resulting mixture was stirred for 2 hours, and was then subjected to dehydration, drying, and powderization. Thus, calcium carbonate (C1) that had been subjected to surface treatment with the fatty acid-based surface treatment agent and had a BET specific surface area (Sw) of 48 m^2/g was obtained. The physical property values of the obtained surface-treated calcium carbonate (C1) are shown in Table 1.

Comparative Example 2: Production of
Surface-Treated Calcium Carbonate (C2)

[0112] Calcium carbonate (C2) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was obtained in the same manner as in Comparative Example 1, except that malic acid was used as a complex-forming agent instead of the citric acid. The physical property values of the obtained surface-treated calcium carbonate (C2) are shown in Table 1.

Comparative Example 3: Production of
Surface-Treated Calcium Carbonate (C3)

[0113] Mixed gas of CO_2 and air containing 20 vol % of CO_2 gas was introduced into the lime milk with a concentration of 5% at a temperature of 10° C. at a flow rate of 1700 L/hour per 1 kg of calcium hydroxide without adding a complex forming agent and an inorganic acid and/or a salt thereof to the lime milk. Thus, a calcium carbonate slurry with a concentration of 10.8% was produced. Subsequently, the calcium carbonate slurry was aged through stirring at a temperature of 30° C. to 35° C. for 30 hours. Then, a 10% aqueous solution of sodium beef tallow fatty acid (fatty acid-based surface treatment agent) obtained through thermal dissolution of the sodium beef tallow fatty acid in warm water was added to the calcium carbonate slurry such that the sodium beef tallow fatty acid solid was 5% of the calcium carbonate solid. The resulting mixture was stirred for 24 hours to allow the surface treatment agent to sufficiently adsorb on the surface of the calcium carbonate, and was then subjected to dehydration, drying, and powderization. Thus, calcium carbonate (C3) that had been subjected to surface treatment with the fatty acid-based surface treatment agent and had a BET specific surface area (Sw) of 17 m^2/g was obtained. The physical property values of the obtained surface-treated calcium carbonate (C3) are shown in Table 1.

Comparative Example 4: Production of
Surface-Treated Calcium Carbonate (C4)

[0114] Calcium carbonate (C4) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was obtained in the same manner as in Example 1, except that the addition amount of the sodium beef tallow fatty acid used as a fatty acid-based surface treatment agent was changed to 5%. The physical property values of the obtained surface-treated calcium carbonate (C4) are shown in Table 1.

Comparative Example 5: Production of
Surface-Treated Calcium Carbonate (C5)

[0115] Calcium carbonate (C5) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was obtained in the same manner as in Example 1, except that a calcium carbonate slurry with a concentration of 16.28% was produced by changing the addition amount of the concentrated sulfuric acid used to 6.0% and changing the concentration of the lime milk to 12%, and this calcium carbonate slurry was aged. The physical property values of the obtained surface-treated calcium carbonate (C5) are shown in Table 1.

Comparative Example 6: Production of
Surface-Treated Calcium Carbonate (C6)

[0116] Calcium carbonate (C6) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was obtained in the same manner as in Example 1, except that the addition amount of the sodium beef tallow fatty acid used as a fatty acid-based surface treatment agent was changed to 25%. The physical property values of the obtained surface-treated calcium carbonate (C6) are shown in Table 1.

Comparative Example 7: Production of
Surface-Treated Calcium Carbonate (C7)

[0117] Calcium carbonate (C7) that had been subjected to surface treatment with the fatty acid-based surface treatment agent was obtained in the same manner as in Example 4, except that the addition amount of the Sodium Palm Fatty Acid used as a fatty acid-based surface treatment agent was changed to 5%. The physical property values of the obtained surface-treated calcium carbonate (C7) are shown in Table 1.

Comparative Example 8: Production of
Surface-Treated Calcium Carbonate (C8)

[0118] Surface-treated calcium carbonate (C8) was obtained in the same manner as in Comparative Example 5, except that sodium oleate was used as a fatty acid-based surface treatment agent instead of the sodium beef tallow fatty acid. The physical property values of the obtained surface-treated calcium carbonate (C8) are shown in Table 1.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1	Comparative Example 2
Name of Surface-Treated Calcium Carbonate Produced	E1	E2	E3	E4	E5	C1	C2
Sw (m^2/g)	45	38	42	46	45	48	48
As (mg/m^2)	2.5	2.6	2.5	2.4	2.6	2.5	2.5
LC (%)	94	94	59	95	94	51	50
Dxp (mm)	0.011	0.013	0.017	0.012	0.011	0.016	0.014
Dyp/Dxp	97	83	60	90	99	86	94
Is ($mmol/m^2$)	1.61	1.66	1.62	1.53	1.64	1.6	1.6
(1)Lime Milk Conc.(%)	5	5	7	5	5	8	8
(2)Lime Milk Additive	Sulphric Acid	Sulphric Acid	Citric Acid	Sulphric Acid	Sulphric Acid	Citric Acid	Malic Acid
Conc. of Addtive	4.5	3.0	2.0	4.5	4.5	3	3
(3)Carbon Dioxide Gas Amount	1700	1700	1700	1700	1700	1700	1700

TABLE 1-continued

(4)Gas Conc.	20	20	20	20	20	20	20
(5)Calcium Carbonate Conc.	6.8	6.8	9.5	6.8	6.8	10.8	10.8
(6)Maturation Time	30	30	50	30	30	50	50
(7)Surface Treatment Amount	14	12	13	14	14	15	15
(8)Surface Treatment Time	2	2	24	2	2	2	2
(9)Surface Treatment Agent	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid	Sodium Palm Fatty Acid	Sodium Oleate	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid

	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Name of Surface-Treated Calcium Carbonate Produced	C3	C4	C5	C6	C7	C8
Sw (m²/g)	17	49	40	41	51	39
As (mg/m²)	2.6	0.89	2.8	4.5	0.82	2.9
LC (%)	95	95	94	93	95	94
Dxp (mm)	0.039	0.045	0.012	0.010	0.047	0.011
Dyp/Dxp	33	26	42	53	25	41
Is (mmol/m²)	1.65	0.57	1.81	2.88	0.53	1.89
(1)Lime Milk Conc.(%)	5	5	12	5	5	12
(2)Lime Milk Additive	None	Sulphric Acid	Sulphric Acid	Sulphric Acid	Sulphric Acid	Sulphric Acid
Conc. of Addtive	—	4.5	6.0	4.5	4.5	6.0
(3)Carbon Dioxide Gas Amount	1700	1700	1700	1700	1700	1700
(4)Gas Conc.	20	20	20	20	20	20
(5)Calcium Carbonate Conc.	6.8	6.8	16.2	6.8	6.8	16.2
(6)Maturation Time	30	30	50	30	30	50
(7)Surface Treatment Amount	5	5	14	25	5	14
(8)Surface Treatment Time	24	2	2	2	2	2
(9)Surface Treatment Agent	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid	Sodium Beef Tallow Fatty Acid	Sodium Palm Fatty Acid	Sodium Oleate

Examples 6 to 10 and Comparative Examples 9 to 16: Production and Evaluation of Sealants

[0119] The surface-treated calcium carbonates (E1) to (E5) and (C1) to (C8) produced in Examples 1 to 5 and Comparative Examples 1 to 8 above were used to produce one component-type polyurethane-based sealants based on the composition below, and various properties thereof were evaluated. The results are shown in Table 2 and Table 3.

Composition

[0120] Polyurethane resin Takenate L-1036 (manufactured by Mitsui Takeda Chemicals, Inc.) 430 parts

[0121] Heavy calcium carbonate (Super S, manufactured by Maruo Calcium Co., Ltd.) 230 parts

[0122] Surface-treated calcium carbonate produced in each of the examples and the comparative examples above 150 parts

[0123] Mineral turpentine 100 parts

Kneading Method

[0124] The polyurethane resin was charged into a 5-L universal mixing-stirring machine (manufactured by Dalton Corporation), and the surface-treated calcium carbonate produced in each of the examples and the comparative examples above and the heavy calcium carbonate were dried at 105° C. for 2 hours or more in advance and were then simultaneously charged thereinto. Then, the resulting mixture was preliminarily stirred at a low speed for 15 minutes. Thereafter, the blend adhering to the inside of the mixing-stirring machine was scraped off and was immediately kneaded at a high speed for 30 minutes in a vacuum atmosphere. Finally, the mineral turpentine was charged and mixed at a low speed for 15 minutes in a vacuum atmosphere. A cartridge laminated with an aluminum foil was filled with the resulting mixture and was hermetically sealed using a metal plunger. Thus, a one component-type polyurethane sealant was produced.

Viscosity Measurement Method

[0125] The above-mentioned sealant that had been allowed to stand at 23° C. for 1 day was filled into a 100-mL PP (polypropylene) cup using a cartridge gun, and the viscosities at 1 rpm and 10 rpm were measured using a TV-type viscometer (VISCOMETER TV-100BH, manufactured by Toki Sangyo) and were taken as initial viscosities of the sealant (range AH, spindle No. H7). In the case of 1 rpm, the value obtained after 3 minutes was taken as the viscosity value, and in the case of 10 rpm, the value obtained after 1 minute was taken as the viscosity value. A value obtained by dividing the viscosity value at 1 rpm by the viscosity value at 10 rpm was defined as a TI value.

[0126] After the cartridge filled with the sealant was allowed to stand at 50° C. for 7 days and was then allowed to cool at 23° C. for 3 hours, the viscosities were measured in the same manner as described above and were taken as the viscosity values and the TI value of the sealant after storage.

Criteria for Sealant Viscosity

[0127] The viscosity was evaluated using the following criteria based on the TI value (1 rpm viscosity value/10 rpm viscosity value).

[0128] A: 6.0 or more
[0129] B: 5.5 or more and less than 6.0
[0130] C: 5.0 or more and less than 5.5
[0131] D: Less than 5.0

Storage Stability Test

[0132] The viscosity change rates and the TI value change rate were calculated based on the formulae below using the initial viscosity values measured after the sealant was allowed to stand at 23° C. for 1 day and the viscosity values after storage measured after the sealant was allowed to stand at 50° C. for 7 days (and was then allowed to cool at 23° C. for 3 hours), and the storage stability (rate of change: %) was evaluated.

$$\text{1 rpm viscosity change} \quad (1)$$
$$\text{ratio} = \left[(\text{viscosity value at 1 rpm after storage})/\right.$$
$$\left.(\text{initial visosity value at 1 rpm})\right] \times 100$$

$$\text{10 rpm viscosity change} \quad (2)$$
$$\text{ratio} = \left[(\text{viscosity value at 10 rpm after storage})/\right.$$
$$\left.(\text{initial visosity value at 10 rpm})\right] \times 100$$

$$\text{TI value change} \quad (3)$$
$$\text{ratio} = \left[(\text{TI value after storage})/(\text{initial TI value})\right] \times 100$$

Criteria for Storage Stability

[0133] The storage stability was evaluated using the following criteria based on the viscosity change ratios and the TI value change ratio.
[0134] A: The viscosity change ratios were less than 120% and the TI value change rate was 95% or more.
[0135] B: The viscosity change ratios were 120% or more and less than 140% and the TI value change rate was 90% or more and less than 95%.
[0136] C: The viscosity change ratios were 140% or more and less than 150% and the TI value change rate was 80% or more and less than 90%.
[0137] D: The viscosity change ratios were 150% or more and the TI value change rate was less than 80%.

Tensile Test Method

[0138] After a primer was applied onto the surface of an aluminum plate (50 mm×50 mm×3 mm) and was dried for 60 minutes, the above-mentioned sealant was filled (into a shape with 12 mm×12 mm×50 mm) to produce an H-type specimen based on JIS A 1439 Sealing Material for Building 5.12.2 Durability, Production of Specimen.
[0139] After this specimen was cured at 23° C. for 14 days and then at 35° C. for 14 days, and was allowed to stand at 23° C. for 1 day, initial tensile test values were measured using a tensile tester (Autograph AG-1, manufactured by Shimadzu Corporation).
[0140] The evaluation items in Table 3 were as follows.
[0141] "50% Tensile Stress": a value obtained by dividing a load when the specimen was drawn at a rate of 50 mm/minute and elongated until the elongation rate reaches 50% (6 mm) by the cross-sectional area of the sealant (600 mm²).

[0142] "Maximum Strength": a value obtained by dividing the maximum load when the specimen was drawn at a rate of 50 mm/minute by the cross-sectional area of the sealant.
[0143] "Elongation Rate": a value obtained by dividing the amount of displacement at the time of the measurement of the maximum strength by the shape (12 mm) at the time of filling and multiplying the obtained value by 100.
[0144] "Adhesiveness (initial)": evaluated using the ratio of the adhesive area of the sealant remaining on the aluminum plate when the sealant was broken at the time of the tensile test performed after the sealant had been cured at 23° C. for 14 days and then at 35° C. for 14 days, and had been allowed to stand at 23° C. for 1 day.

Criteria for Tensile Test

[0145] "50% Tensile Stress"
[0146] A: less than 0.20 N/mm².
[0147] B: 0.20 N/mm² or more.
[0148] "Maximum Strength"
[0149] A: 1.00 N/mm² or more.
[0150] B: 0.80 N/mm² or more and less than 1.00 N/mm².
[0151] C: 0.70 N/mm² or more and less than 0.80 N/mm².
[0152] D: less than 0.70 N/mm².
[0153] "Elongation Rate"
[0154] A: 800% or more.
[0155] B: 700% or more and less than 800%.
[0156] C: 600% or more and less than 700%.
[0157] D: less than 600%.
[0158] "Adhesiveness"
[0159] The state in which the sealant remained on the aluminum adhesive surface was represented by the ratio of cohesive failure (the ratio of the remaining adhesive area; CF %), and was evaluated using the following criteria.
[0160] A: The sealant was broken in a state in which 100% remained (CF100%).
[0161] B: The sealant was broken in a state in which 80% or more and less than 100% remained (CF50% to CF99%).
[0162] C: Less than 80% of the sealant remained (CF<80%) or the sealant peeled off (AF).

Tensile Test Method after Heating

[0163] An H-type specimen was produced in the same manner as in the tensile test above. After being cured at 23° C. for 14 days and then 35° C. for 14 days, the specimen was subjected to high-temperature treatment at 100° C. for 14 days. After the specimen was allowed to cool at 23° C. for 1 day, the same tensile test was performed, and thus a tensile test values after heating were obtained.

Thermal Stability Test

[0164] The change rates were calculated using the following formulae based on the initial tensile test values and the tensile test values after heating, and the thermal stability (rate of change: %) was evaluated.

$$\text{50\% tensile stress change ratio} = \left[(\text{50\% tensile stress after heating})/\right. \quad (1)$$
$$\left.(\text{initial 50\% tensile stress})\right] \times 100$$

-continued

Maximum strength change   (2)

$$ratio =: [(\text{maximum strength after heating})/(\text{initial maximum strength})] \times 100$$

Elongation change   (3)

$$ratio = [(\text{elongation rate after heating})/(\text{initial elongation rate})] \times 100$$

Criteria for Thermal Stability

[0165] The thermal stability was evaluated using the following criteria based on the 50% tensile stress change ratio, the maximum strength change ratio and the elongation change ratio.

[0166] A: The 50% tensile stress change ratio and the maximum strength change ratio were less than 140%, and the elongation change ratio was 85% or more.

[0167] B: The 50% tensile stress change ratio and the maximum strength change ratio were 140% or more and less than 180%, and the elongation change ratio was 80% or more and less than 85%.

[0168] C: The 50% tensile stress change ratio and the maximum strength change ratio were 180% or more and less than 220%, and the elongation change ratio was 70% or more and less than 80%.

[0169] D: The 50% tensile stress change ratio and the maximum strength change ratio were 220% or more, and the elongation change ratio was less than 70%.

TABLE 2

| | Name of Surface- | | Sealant Viscosity | | | | Storage Stability | | |
| | Treated | | | | | | 1 rpm | 10 rpm | |
	Calcium Carbonate Used		1 rpm (Pa · s)	10 rpm (Pa · s)	TI Value (1 rpm/ 10 rpm)	Evaluaton	Viscosity Change Ratio	Viscosity Change Ratio	TI Value Change Ratio
Example 6	E1	Initial	1250	210	6.0	A	117	126	93
		After Storage	1460	265	5.5	B	A	B	B
Example 7	E2	Initial	1020	169	6.0	A	113	119	95
		After Storage	1150	201	5.7	B	A	A	A
Example 8	E3	Initial	1000	172	5.8	B	137	148	92
		After Storage	1370	255	5.4	C	B	C	B
Example 9	E4	Initial	1230	204	6.0	A	115	123	94
		After Storage	1410	250	5.6	B	A	B	B
Example 10	E5	Initial	1250	206	6.1	A	116	125	93
		After Storage	1450	258	5.6	B	A	B	B
Comparative Examole 9	C1	Initial	1310	221	5.9	B	143	182	78
		After Storage	1870	402	4.7	D	C	D	D
Comparative Examole 10	C2	Initial	1340	218	6.1	A	141	178	79
		After Storage	1890	388	4.9	D	C	D	D
Comparative Examole 11	C3	Initial	430	120	3.6	D	109	112	97
		After Storage	468	134	3.5	D	A	A	A
Comparative Examole 12	C4	Initial	510	110	4.6	D	135	152	89
		After Storage	688	167	4.1	D	B	D	C
Comparative Examole 13	C5	Initial	790	163	4.8	D	115	128	90
		After Storage	910	209	4.4	D	A	B	B
Comparative Examole 14	C6	Initial	1540	310	5.0	C	168	193	87
		After Storage	2590	598	4.3	D	D	D	C
Comparative Examole 15	C7	Initial	503	108	4.7	D	134	150	89
		After Storage	675	162	4.2	D	B	D	C
Comparative Examole 16	C8	Initial	800	168	4.8	D	115	127	91
		After Storage	920	213	4.3	D	A	B	B

TABLE 3

| | Name of Surface- | Initial Tensile Test | | | | | | |
	Treated Calcium Carbonate Used	50% Tensile Stress (N/mm²)	Evaluation	Maximun Strength (N/mm²)	Evaluation	Elongation Rate (%)	Evaluation	Adhesiveness
Example 6	E1	0.14	A	1.06	A	840	A	100
Example 7	E2	0.14	A	1.18	A	770	B	100
Example 8	E3	0.15	A	1.00	A	780	B	100
Example 9	E4	0.13	A	1.07	A	880	A	100
Example 10	E5	0.13	A	1.07	A	850	A	100
Comprative Example 9	C1	0.13	A	1.07	A	860	A	100

TABLE 3-continued

Comparative Example 10	C2	0.13	A	1.07	A	880	A	100
Comparative Example 11	C3	0.09	A	0.81	B	520	D	70
Comparative Example 12	C4	0.45	B	0.63	D	390	D	60
Comparative Example 13	C5	0.18	A	0.74	C	600	C	90
Comparative Example 14	C6	0.10	A	0.78	C	670	C	100
Comparative Example 15	C7	0.42	B	0.68	D	410	D	60
Comparative Example 16	C8	0.17	A	0.76	C	620	C	90

		Tensile Test After Heating			Thermal Stability 50%		
	Initial Tensile Test Evaluation	50% Tensile Stress (N/mm²)	Maximun Strength (N/mm²)	Elongation Rate (%)	Tebsile Stress Change Ratio	Maximun Strength Change Ratio	Elongation Change Ratio
Example 6	A	0.24	1.44	700	171 B	136 A	83 B
Example 7	A	0.23	1.55	660	164 B	131 A	86 A
Example 8	A	0.28	1.48	620	187 C	148 B	79 C
Example 9	A	0.22	1.4	720	169 B	131 A	84 B
Example 10	A	0.23	1.45	700	177 B	136 A	82 B
Comprative Example 9	A	0.33	2.12	500	254 D	198 C	58 D
Comparative Example 10	A	0.32	2.03	520	246 D	190 C	59 D
Comparative Example 11	C	0.13	1.03	400	144 B	127 A	77 C
Comparative Example 12	C	0.63	0.76	230	140 B	121 A	59 D
Comparative Example 13	B	0.33	1.08	510	183 C	146 B	85 A
Comparative Example 14	A	0.21	1.34	520	210 C	172 B	78 C
Comparative Example 15	C	0.59	0.8	250	140 B	118 A	61 D
Comparative Example 16	B	0.32	1.08	530	188 C	142 B	85 A

[0170] As shown in Table 2, it can be seen that all the sealants (Examples 6 to 10) in which the surface-treated calcium carbonates (E1) to (E5) produced in Examples 1 to 5 were used had a good initial sealant viscosity and a good sealant viscosity after storage and excellent storage stability, compared with the sealants (Comparative Examples 9 to 16) in which the surface-treated calcium carbonates (C1) to (C8) produced in Comparative Examples 1 to 8 were used.

[0171] Also, as shown in Table 3, it can be seen that all the sealants (Examples 6 to 10) in which the surface-treated calcium carbonates (E1) to (E5) produced in Examples 1 to 5 were used had a sufficient elongation rate even in the tensile test after heating and excellent thermal stability, compared with the sealants (Comparative Examples 9 to 16) in which the surface-treated calcium carbonates (C1) to (C8) produced in Comparative Examples 1 to 8 were used.

Examples 11 to 15 and Comparative Examples 17 to 24: Production and Evaluation of Plastisols

[0172] The surface-treated calcium carbonates (E1) to (E5) and (C1) to (C8) produced in Examples 1 to 5 and Comparative Examples 1 to 8 above were used to produce plastisols (vinyl chloride paste sols) based on the composition below, and various properties thereof were evaluated. The results are shown in Table 4.

Composition

[0173] Vinyl chloride paste resin PCH-843 (manufactured by Kaneka Corporation) 250 parts

[0174] Polyamide (manufactured by Henkel Japan Ltd.) 15 parts

[0175] Diisononyl phthalate (DINP) 250 parts

[0176] Quicklime (manufactured by FUJIFILM Wako Pure Chemical Corporation) 15 parts

[0177] Turpentine 37 parts

[0178] Surface-treated calcium carbonate produced in each of the examples and the comparative examples above 160 parts

[0179] Heavy calcium carbonate (Super S, manufactured by Maruo Calcium Co., Ltd.) 90 parts

Kneading Method

[0180] Each blend was charged into a 5-L universal mixing-stirring machine (manufactured by Dalton Corporation) and kneaded for 3 minutes. The lid of the stirring machine was opened once, and the blend adhering to the wall surface was scraped off. Then, the blend was kneaded again for 10 minutes in a vacuum atmosphere. The kneaded sol was defoamed in a planetary defoaming kneader (KK-1000W, manufactured by Kurabo Industries Ltd.) under a kneading condition of May 5, 2018, and thus a vinyl chloride sol was produced. Note that, in the kneading condition "a-b-c" above, "a" represents a revolution condition, "b" represents a rotation condition, and "c" represents time (c×10 seconds).

Viscosity Measurement

[0181] The kneaded plastisol was filled into a 100-mL PP (polypropylene) cup and was allowed to stand at 23° C. for 3 days. Then, the viscosities at 2 rpm and 20 rpm were measured as initial viscosities using a TV-type viscometer (VISCOMETER TV-100BH, manufactured by Toki Sangyo) (range AH, spindle No. H7).

[0182] In the case of the 2 rpm viscosity, the value obtained after 2 minutes was taken as the viscosity value, and in the case of 20 rpm, the value obtained after 1 minute was taken as the viscosity value. A value obtained by dividing the 2 rpm viscosity value by the 20 rpm viscosity value was used to represent the TI value. Furthermore, the kneaded plastisol filled into a 100-mL PP cup was allowed to stand at 40° C. for 3 days and was then allowed to cool at 23° C. for 3 hours. Then, the viscosities at 2 rpm and 20 rpm were measured as the viscosities after storage, and the numerical value of 2 rpm viscosity/20 rpm viscosity was measured as the TI value after storage.

Criteria for Sol Viscosity

[0183] The viscosity was evaluated using the following criteria based on the TI value (2 rpm viscosity/20 rpm viscosity).

[0184] A: 6.00 or more.

[0185] B: 5.50 or more and less than 6.00.

[0186] C: 5.00 or more and less than 5.50.

[0187] D: less than 5.00.

Storage Stability Test

[0188] The viscosity change rates and the TI value change rate were calculated based on the formulae below using the initial viscosity values measured after the sol was allowed to stand at 23° C. for 3 days and the viscosity values after storage measured after the sol was allowed to stand at 40° C. for 3 days (and was then allowed to cool at 23° C. for 3 hours), and the storage stability (rate of change: %) was evaluated.

Viscosity change

$$\text{rate} = [(\text{viscosity value at each rotation rate after storage})/$$
$$(\text{initial viscosity value at each rotation rate})] \times 100$$

$$\textit{TI} \text{ value change rate} = [(\textit{TI} \text{ value after storage/initial } \textit{TI} \text{ value})] \times 100$$

Criteria for Storage Stability

[0189] The storage stability was evaluated using the following criteria based on the viscosity change rates and the TI value change rate.

[0190] A: The viscosity change rates were less than 105% and the TI value change rate was 95% or more.

[0191] B: The viscosity change rates were 105% or more and less than 110% and the TI value change rate was 90% or more and less than 95%.

[0192] C: The viscosity change rates were 110% or more and less than 120% and the TI value change rate was 85% or more and less than 90%.

[0193] D: The viscosity change rates were 120% or more and the TI value change rate was less than 85%.

Electrodeposition Plate Adhesion Test Method

[0194] The kneaded plastisol was applied onto a sufficiently polished steel plate with a size of 70 mm×150 mm such that the thickness of the plastisol was 3 mm. The plastisol was baked and cured for 30 minutes in an incubator at 100° C., and was exposed to normal temperature for 15 minutes and cooled. Then, the plastisol was allowed to stand at 130° C. for 30 minutes and was allowed to cool at normal temperature for 15 minutes. This operation was repeated twice. After being cooled, the cured coating was scraped with a nail, and the state in which the cured coating remained on the electrodeposition plate was represented by the ratio of cohesive failure (the ratio of the remaining adhesive area; CF %). The adhesion was thus confirmed, and was evaluated using the following criteria.

Criteria for Electrodeposition Plate Adhesion

[0195] A: The cured coating had excellent adhesion, and when being scraped, the cured coating was broken (CF100%) in a state in which all the cured coating remained on the electrodeposition plate.

[0196] B: The cured coating had excellent adhesion, but when being scraped, the cured coating was broken (70%≤CF<100%) in a state in which 70% or more and less than 100% of the cured coating remained on the electrodeposition plate.

[0197] C: The cured coating easily peeled off, and when being scraped, the cured coating was broken (CF<70%) in a state in which only less than 70% of the cured coating remained on the electrodeposition plate.

TABLE 4

	Name of Surface-Treated Calcium Carbonate Used		Sol Viscosity				Storage Stability			Electrodeposition Plate Adhesion (CF %)
			2 rpm (Pa · s)	20 rpm (Pa · s)	TI Value (2 rpm/ 20 rpm)	Evaluation	2 rpm Change Rate	20 rpm Change Rate	TI Change Rate	
Example 11	E1	Initial	951	152.2	6.2	A	103	108	96	100
		After Storage	978	163.7	6.0	A	A	B	A	A
Example 12	E2	Initial	875	138.5	6.3	A	101	103	99	100
		After Storage	887	142.4	6.2	A	A	A	A	A
Example 13	E3	Initial	903	148.6	6.1	A	105	111	95	80
		After Storage	946	164.3	5.8	B	B	C	A	B
Example 14	E4	Initial	985	157.6	6.3	A	101	105	97	100
		After Storage	998	164.8	6.1	A	A	B	A	A
Example 15	E5	Initial	932	149.3	6.2	A	103	106	96	100
		After Storage	956	158.8	6.0	A	A	B	A	A
Comprative Example 17	C1	Initial	936	146.5	6.4	A	111	125	89	50
		After Storage	1040	182.8	5.7	B	C	D	C	C
Comparative Example 18	C2	Initial	928	141.8	6.5	A	111	119	93	50
		After Storage	1030	169.4	6.1	A	C	C	B	C
Comparative Example 19	C3	Initial	287	74.5	3.9	D	108	106	103	100
		After Storage	311	78.7	4.0	D	B	B	A	A
Comparative Example 20	C4	Initial	336	87.3	3.8	D	103	106	97	100
		After Storage	346	92.6	3.7	D	A	B	A	A
Comparative Example 21	C5	Initial	528	97.4	5.4	C	106	109	97	70
		After Storage	562	106.5	5.3	C	B	B	A	B
Comparative Example 22	C6	Initial	648	113.1	5.7	B	113	120	95	50
		After Storage	735	135.6	5.4	C	C	D	A	C
Comparative Example 23	C7	Initial	348	88.5	3.9	D	102	106	97	100
		After Storage	356	93.4	3.8	D	A	B	A	A
Comparative Example 24	C8	Initial	521	95.7	5.4	C	105	107	98	80
		After Storage	548	102.2	5.4	C	B	B	A	B

[0198] As shown in Table 4, it can be seen that all the plastisols (Examples 11 to 15) in which the surface-treated calcium carbonates (E1) to (E5) produced in Examples 1 to 5 were used had a good initial sol viscosity and a good sol viscosity after storage, excellent storage stability, and excellent adhesion to the electrodeposition plate, compared with the plastisols (Comparative Examples 17 to 24) in which the surface-treated calcium carbonates (C1) to (C8) produced in Comparative Examples 1 to 8 were used.

Examples 16 to 20 and Comparative Examples 25 to 32: Production and Evaluation of Paint Compositions

[0199] The surface-treated calcium carbonates (E1) to (E5) and (C1) to (C8) produced in Examples 1 to 5 and Comparative Examples 1 to 8 above were used to produce paint compositions based on the composition below, and various properties thereof were evaluated. The results are shown in Table 5.

Composition

[0200] Mineral spirit 90 parts

[0201] Long-oil alkyd resin (oil length of 65%/NV70) 240 parts

[0202] Titanium oxide 140 parts

[0203] Surface-treated calcium carbonate produced in each of the examples and the comparative examples above 25 parts

[0204] Mixed dryer 5 parts

[0205] Anti-skinning agent 1 part

[0206] Glass beads 500 parts

Preparation Method

[0207] The above-mentioned blend was dispersed using an SG mill to 10 μm or less on a grain gauge basis. Then, the glass beads were removed, and the resulting paint composition was placed in a paint can (200 mL). The paint can was hermetically sealed and was allowed to stand at 23° C. for 1 day. Thereafter, various physical properties were measured and evaluated according to the methods below.

KU Value

[0208] The KU value of the paint composition in the paint can was measured using a krebs stormer viscometer (STOMER'S VISCOMETER, manufactured by Ueshima Seisakusho Co., Ltd.).

Thixotropy

[0209] The viscosities of the paint composition in the paint can at 6 rpm and 60 rpm were measured using a TV-type viscometer (VISCOMETER TV-100BH, manufactured by Toki Sangyo) and were taken as initial viscosities (range AH, spindle No. H7). In both cases of 6 rpm and 60 rpm, the value obtained after 1 minute was taken as the viscosity value, and a value obtained by dividing the 6 rpm viscosity value by the 60 rpm viscosity value was defined as a TI value.

Criteria for Thixotropy

[0210] The thixotropy was evaluated using the following criteria based on the obtained TI value (6 rpm viscosity value/60 rpm viscosity value).

[0211] A: 3.0 or more.

[0212] B: 2.5 or more and less than 3.0.

[0213] C: 2.0 or more and less than 2.5.
[0214] D: less than 2.0.

Sagging Properties

[0215] The KU viscosity value of each paint composition was adjusted to 70 by adding mineral spirit, and then the paint composition was applied to all-black measurement paper using 250 μm, 200 μm, 150-μm, and 100-μm applicators. Immediately after the application, the paper was leaned against something such that the surface to which the paint composition had been applied extended in a vertical direction, and was allowed to stand at normal temperature for 24 hours. Then, the sagging state of the applied paint was evaluated using the following criteria.
[0216] A: Sagging of the paint was not observed.
[0217] B: Sagging of the paint was observed.

Storage Stability of Paint Composition

[0218] The above-mentioned paint composition whose KU viscosity value was adjusted to 70 with mineral spirit was placed in a paint can (200 mL), and the paint can was hermetically sealed. After the paint can was stored in an oven at 50° C. for 4 weeks, a medicine spoon was used to softly scoop the paint composition on the bottom of the paint can, and it was visually confirmed whether or not a sediment accumulated.

Criteria for Storage Stability

[0219] The storage stability of the paint composition that had been stored while being heated at 50° C. was evaluated using the following criteria.
[0220] A: No sediment was observed.
[0221] B: A sediment was observed.

[0222] As shown in Table 5, it can be seen that all the paint compositions (Examples 16 to 20) in which the surface-treated calcium carbonates (E1) to (E5) produced in Examples 1 to 5 were used had favorable thixotropy, sagging properties, and storage stability, compared with the paint compositions (Comparative Examples 25 to 32) in which the surface-treated calcium carbonates (C1) to (C8) produced in Comparative Examples 1 to 8 were used.

INDUSTRIAL APPLICABILITY

[0223] The present invention is useful in, for example, the resin molding field, the architectural/housing field, the paint field, and a wide range of technical fields related to these fields.

What is claimed is:

1. A surface-treated calcium carbonate comprising calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent,
 wherein the fatty acid-based surface treatment agent is at least one compound selected from the group consisting of fatty acids and fatty acid salts, and
 relational expressions (a) to (f) below are satisfied:

$$20 \le Sw \le 100 \quad (m^2/g) \tag{a}$$

$$1.0 \le As \le 7.5 \quad (mg/m^2) \tag{b}$$

$$LC \ge 55 \quad (\%) \tag{c}$$

$$0.003 \le Dxp \le 0.03 \quad (\mu m) \tag{d}$$

$$50 \le Dyp/Dxp \le 180 \tag{e}$$

$$0.03 \le Is \le 2.57 \quad (\mu mol/m^2). \tag{f}$$

TABLE 5

	Name of Surface-Treated Calcium Carbonate Used	KU Value	Thixotropy				Sagging Properties				Storage Stability
			6 rpm (mPa · s)	60 rpm (mPa · s)	TI Value	Evaluation	250 μm	200 μm	150 μm	100 μm	
Example 16	E1	83	5900	1680	3.5	A	A	A	A	A	A
Example 17	E2	80	4300	1430	3.0	A	A	A	A	A	A
Example 18	E3	81	5200	1600	3.3	A	A	A	A	A	A
Example 19	E4	84	6100	1690	3.6	A	A	A	A	A	A
Example 20	E5	82	5800	1700	3.4	A	A	A	A	A	A
Comparative Example 25	C1	83	6400	1720	3.7	A	A	A	A	A	B
Comparative Example 26	C2	84	6500	1820	3.6	A	A	A	A	A	B
Comparative Example 27	C3	74	1250	640	2.0	C	B	B	B	B	B
Comparative Example 28	C4	76	1320	690	1.9	D	B	B	B	B	B
Comparative Example 29	C5	81	3600	1310	2.7	B	B	B	A	A	A
Comparative Example 30	C6	84	7300	1960	3.7	A	A	A	A	A	A
Comparative Example 31	C7	76	1540	810	1.9	D	B	B	B	B	B
Comparative Example 32	C8	80	3400	1360	2.5	B	B	B	A	A	A

where

Sw is a BET specific surface area (m^2/g) that is determined through a nitrogen adsorption method,

As is loss on heat per unit surface area (mg/m^2) that is determined using the following formula:

$$As = (\text{loss on heat per 1 g of the surface−treated calcium}$$
$$\text{carbonate (mg/g) between 200° C. and 500° C.)}/Sw(m^2/g),$$

LC is a lightness maintenance ratio (%) that is determined using the following formula:

$$LC =$$
$$(\text{an } L \text{ value of a paste obtained by mixing the surface−treated calcium}$$
$$\text{carbonate heated at 160° C. for 12 hours and}$$
$$\text{diisononyl phthalate at a mass ratio of 1 to 2})/$$
$$(\text{an } L \text{ value of a paste obtained by mixing the calcium carbonate prior}$$
$$\text{to heating and diisononyl−phthalate at a mass ratio of 1 to 2}) \times 100,$$

Dxp is an average pore diameter (μm) at which an increase in a mercury intrusion amount (cumulative value of increases in pore volume/log (average pore diameter)) reaches a maximum value (Dyp) in a pore distribution within a pore range of 0.001 to 0.1 μm in a mercury intrusion method,

Dyp is the maximum value of an increase in the mercury intrusion amount (mL/g),

Dyp/Dxp is an average pore diameter amount, and

Is is an alkali metal content per unit specific surface area (μmol/m^2) that is calculated using the following formula:

$$Is = (\text{an alkali metal content per 1 g of the}$$
$$\text{surface−treated calcium carbonate (μmol/g)}/\{Sw(m^2/g)\}.$$

2. The surface-treated calcium carbonate according to claim **1**, wherein the calcium carbonate subjected to surface treatment with a fatty acid-based surface treatment agent satisfies formulae (g) and (h) below:

$$0.005 \le Dxp \le 0.025(\mu m), \text{ and} \tag{g}$$

$$60 \le Dyp/Dxp \le 150. \tag{h}$$

3. A resin composition comprising the surface-treated calcium carbonate according to claim **1**; and a resin.

4. The resin composition according to claim **3**, wherein the resin is a sealant resin.

5. The resin composition according to claim **3**, wherein the resin is an adhesive resin.

6. The resin composition according to claim **3**, wherein the resin is a paint resin.

7. The resin composition according to claim **3**, wherein the resin is a plastisol resin.

8. A resin composition comprising the surface-treated calcium carbonate according to claim **2**; and a resin.

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