



HU000029716T2

(19) **HU****MAGYARORSZÁG**
Szellemi Tulajdon Nemzeti Hivatala(11) Lajstromszám: **E 029 716**(13) **T2****EURÓPAI SZABADALOM**
SZÖVEGÉNEK FORDÍTÁSA

(21) Magyar ügyszám: E 12 176320	(51) Int. Cl.: C09C 1/02	(2006.01)
(22) A bejelentés napja: 2012. 07. 13.	C01F 11/18	(2006.01)
	C09C 3/06	(2006.01)
(96) Az európai bejelentés bejelentési száma: EP 20120176320	C09C 3/08	(2006.01)
(97) Az európai bejelentés közzétételi adatai: EP 2684916 A1 2014. 01. 15.	D21H 15/02	(2006.01)
(97) Az európai szabadalom megadásának meghirdetési adatai: EP 2684916 B1 2016. 04. 27.	D21H 17/00	(2006.01)
	D21H 17/15	(2006.01)
	D21H 17/67	(2006.01)
	D21H 17/69	(2006.01)
	D21H 19/38	(2006.01)
	D21H 21/52	(2006.01)

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(54) **Felületmódosított kalcium-karbonátot tartalmazó ásványok és azok alkalmazása**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.



(11) **EP 2 684 916 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
27.04.2016 Bulletin 2016/17

(21) Application number: **12176320.5**

(22) Date of filing: **13.07.2012**

(51) Int Cl.:
C09C 1/02 ^(2006.01) **D21H 17/00** ^(2006.01)
D21H 15/02 ^(2006.01) **D21H 17/67** ^(2006.01)
D21H 19/38 ^(2006.01) **D21H 21/52** ^(2006.01)
C01F 11/18 ^(2006.01) **C09C 3/06** ^(2006.01)
C09C 3/08 ^(2006.01) **D21H 17/15** ^(2006.01)
D21H 17/69 ^(2006.01)

(54) **SURFACE MODIFIED CALCIUM CARBONATE CONTAINING MINERALS AND ITS USE**

OBERFLÄCHENMODIFIZIERTES CALCIUMCARBONAT MIT MINERALIEN UND SEINE
VERWENDUNG

CARBONATE DE CALCIUM À SURFACE MODIFIÉE CONTENANT DES MINÉRAUX ET SON
UTILISATION

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME

(43) Date of publication of application:
15.01.2014 Bulletin 2014/03

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US-A1- 2006 162 884 **US-B1- 6 666 953**

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DescriptionField of the Invention

[0001] The present invention is related to calcium carbonate containing minerals, and in particular to ball-shaped spherical surface modified spherical calcium carbonate comprising mineral particles with a mean particle size diameter above 1 μm , and its use. A particular use is in paints and coatings, providing for a surface matting effect of the paint and coating while at the same time providing for a smooth paint or coating surface.

Background of the Invention

[0002] The present invention is directed to modified calcium carbonate containing minerals and their use, e.g., in paints and coatings at low dosage, and more particularly to a modified calcium carbonate containing mineral providing a matting effect in paints and coatings, while at the same time providing a smooth paint or coating film.

Today matting effects can be achieved by different means as long as they provide for a micro-roughness of the paint or coating film surface, wherein the incident light is scattered in a way that results in matted surface. The physics behind this is known.

The conditions to obtain a perfectly matted effect without resorting to complete light absorption are to scatter the incoming light away from the specular reflectance angle. This means diffracting the directed light that illuminates the substrate causing diffuse scatter.

[0003] In paint and coating industries a variety of such matting agents are known and mixed into the paints and coatings such as silica, waxes, organic materials and even fillers are added to form a micro-rough surface after the drying process of the paint or coating. It is recognized as a general rule that the higher the dosing of the matting agent in a paint or coating, the stronger the matting effect. In contrast, products with larger particle sizes are stronger in matting efficiency but the resulting paint or coating film surface is not so smooth. Matting agents with smaller average particle size distribution do not provide sufficient matting effect, but provide for a smoother paint or coating surface.

[0004] Japanese patent application JP-A-2003 147275 discloses a coating material composition comprising a binder component and a calcium carbonate treated with phosphoric acid. Said coating material provides for a matte surface providing that the treated calcium carbonate has a mean particle diameter of less than 10 μm , a BET specific surface area of 70-100 m^2/g and oil absorption of 130-20 $\text{ml}/100\text{g}$.

[0005] WO 2006/105189 A1 refers to aggregated particulate minerals and compositions comprising aggregated calcium carbonate. Said dry aggregated calcium carbonate beads have a weight median aggregate particle size d_{50} of at least 5 μm and even a size of at least 100 μm . Said aggregated calcium carbonate beads are made into paper, paint, coatings or ceramics.

[0006] US 5,634,968 refers to carbonate containing mineral fillers, more particularly for use as matting agents. Said mineral materials are natural and/or precipitated calcium carbonates with a d_{50} of 9.6-20.5 μm , wherein ground natural calcium carbonates are preferred.

[0007] US 5,531,821 and US 5,584,923 disclose and claim acid resistant calcium carbonates made by mixing calcium carbonate with anionic salts and cationic salts. Said acid resistant calcium carbonate is being used in neutral to weakly acid paper making processes.

[0008] US 6,666,953 disclose a pigment of filler containing natural carbonate which is treated with one or more providers of medium-strong to strong H_3O^+ ions and gaseous CO_2 .

[0009] US 2008/0022901 refers to mineral pigments containing a dry product formed in situ by the multiple reaction between a calcium carbonate and the product or products of reaction of said carbonate with one or more moderately strong to strong H_3O^+ ion donors and the product or products of reaction of the said calcium carbonate with gaseous CO_2 formed in situ and/or originating from an external supply and one or more compounds of formula R-X.

[0010] EP 2 264 109 A1 and EP 2 264 108 A1 disclose a process for preparing a surface - reacted calcium carbonate and its use as well as a process to prepare a surface-reacted calcium carbonate implementing the a weak acid, resulting products and uses thereof. A process for producing a ball-shaped calcium carbonate involving the use of a processing agent is not disclosed in said documents.

[0011] US 2006/0162884 A1 relates to a mineral pigment containing calcium carbonate characterized in that it contains a product formed in situ by the double and/or multiple reaction between a calcium carbonate and the reaction product or products of said carbonate with gaseous CO_2 formed in situ and/or coming from an external supply. EP 0 179 597 B1 describes a precipitated calcite having particles of spherical morphology with an average spherical diameter of from 2 to 10 micrometers, particles distribution such that at least 50 weight percent of the particles lie within plus and minus 50 percent of the average spherical diameter, and a specific surface area of from 1 to 15 square meters per gram.

Description of the Invention

[0012] The present invention relates to a surface modified calcium carbonate comprising mineral of spherical shape as defined in claims 16 and 21, and its use. Particularly they are used in paints or coatings, providing for a matting effect and a smooth paint or coating surface at low dosage. Surface modified calcium carbonate comprising mineral can be obtained by processes as described in the prior art.

[0013] The process for producing the spherical shaped surface modified calcium carbonate comprising particles comprises the steps of:

- a) providing at least one aqueous calcium carbonate containing mineral slurry;
- b) providing at least one water-soluble acid;
- c) optionally providing further gaseous CO₂ via an external route;
- d) contacting said aqueous calcium carbonate containing mineral slurry of step a) with said acid of step b) and with said CO₂ generated in situ and/or supplied externally of step c) under stirring conditions.
- e) optionally dewatering the aqueous slurry;

wherein the at least one processing agent is added before, during or after said aqueous calcium carbonate containing mineral slurry of step a) is contacted with said acid of step b) and with said CO₂ generated in situ and/or supplied externally of step c), and

wherein the at least one processing agent is selected from the group consisting of ferrous sulfate, ferric sulfate, ferrous chloride, ferric chloride, aluminum sulfate, and/or their hydrated forms, and

wherein the processing agent is added in amounts of up to 8 wt.% based on the dry weight of the slurry.

[0014] The spherical ball-shaped surface modified calcium carbonate containing mineral obtained by such a process has specific BET surface area of more than 15 m²/g, and preferably from about 20 m²/g to about 200 m²/g, more preferably from about 30 m²/g to about 150 m²/g, even more preferably from about 40 m²/g to about 100 m²/g, and a median grain diameter of from about 4 μm to about 100 μm, preferably from about 5 μm to about 75 μm, more preferably from about 1 μm to about 50 μm, still more preferably from about 15 μm to about 30 μm.

[0015] Within the context of the present invention, spherical shaped means that the appearance of the spherical shaped surface modified calcium carbonate containing mineral is globular or ball-shaped.

[0016] Further, the ball-shaped surface modified calcium carbonate comprising mineral has a narrow particle size distribution d_{98}/d_{50} preferably smaller than 3, more preferably smaller than 2.5, preferably in a range from 1.4 to 2.9.

[0017] These specific properties are particularly obtained when the at least one aqueous calcium carbonate containing mineral slurry has a solids content of greater than 4 wt.-%, preferably from 5 wt.-% to about 20 wt.-%, more preferably from about 7 wt.-% to about 10 wt.-%, based on the weight of the slurry. Lower solids content such as below 4 wt.-% or higher solids content such as above 20 wt.-% could be used as well.

[0018] It is preferred that the calcium carbonate containing mineral is selected from the group consisting of marble, chalk, limestone, calcite, dolomite and precipitated calcium carbonate (PCC), and mixtures thereof. PCC is sometimes also referred to as synthetic calcium carbonate. Said calcium carbonate containing mineral are basically supplied in an aqueous system. Said aqueous system frequently being a slurry.

[0019] A "slurry" in the meaning of the present invention is a suspension (comprising essentially insoluble solids and water and optionally further additives) and usually has a higher density than the liquid without solids from which it is formed.

[0020] In accordance with the present invention the calcium carbonate containing mineral comprises generally either ground marble, chalk, limestone, calcite, dolomite or mixtures thereof, but encompasses also precipitated calcium carbonate (PCC), which is also known as synthetic calcium carbonate as starting material.

[0021] Advantageously, the calcium carbonate containing mineral present in the slurry has a weight median particle diameter of 0.01 μm to 10 μm, preferably from 0.2 μm to 2 μm, more preferably from 0.5 μm to 1 μm, as measured by Sedigraph.

[0022] The slurry in the process of the present invention can be stabilized or not. In case the slurry is stabilized, conventional dispersants known to the skilled person can be used. A preferred dispersant is polyacrylic acid, or other partially or fully neutralized forms like sodium polyacrylate.

[0023] The at least one water-soluble acid provided in step b) can be chosen from acids as disclosed in EP 2 264 109 A1 and/or EP 2 264 108 A1. An example of such acid is phosphoric acid or sulfuric acid.

[0024] The at least one water-soluble acid provided in step b) is dosed in a molar amount relative to the numbers of moles of the calcium carbonate containing mineral in the range from 0.01 mol/mol to about 1 mol/mol. Preferably from 0.1 to 0.6 mol/mol.

[0025] The at least one water-soluble acid provided in step b) is added in one or more steps, preferably in one step to said aqueous calcium carbonate containing mineral slurry.

[0026] The addition in one or more steps can also be executed over a defined time period, such as a time period of

5 min, 10 min, 20 min, 30 min, 60 min or longer such as 120 min or 180 min. When the addition is made over a certain time period, the addition can be made continuously or discontinuously. E.g. adding 30 % dose over 10 minutes would therefore be 3 % dose per minute.

[0027] Optionally, after the addition of at least one water-soluble acid in step b) gaseous CO₂ can be provided into the slurry by an external route. Such addition of gaseous CO₂ is known to the skilled person. However CO₂ can be generated also in situ when the carbonate containing mineral is reacting with the H₃O⁺ ions. Therefore the origin of CO₂ can be either in situ or supplied externally or even a combination thereof.

[0028] Irrespective of the optional addition of gaseous CO₂ to the slurry, the process of the present invention further comprises the step e) which is contacting said aqueous calcium carbonate containing mineral slurry of step a) with said acid of step b) and with said in situ generated and/or externally supplied CO₂ of step d), said contacting being made under stirring or mixing conditions.

[0029] The process further comprises a step wherein a processing agent is provided before, during or after the at least one aqueous calcium carbonate containing mineral slurry of step a) is contacted with said at least one water-soluble acid of step b) and with said in situ generated or externally supplied CO₂ or a combination thereof of step d).

[0030] Preferably the processing agent is provided before and/or during the at least one aqueous calcium carbonate containing mineral slurry of step a) is contacted with said at least one water-soluble acid of step b) and with said in situ generated or externally supplied CO₂ or a combination thereof of step d).

[0031] Thus, in a particular embodiment of the process as herein disclosed, the processing agent is added before the addition of the water-soluble acid of step b), followed by the steps c), d), and e)

[0032] In a further particular embodiment of the process as herein disclosed, the processing agent is added during the addition of the water-soluble acid of step b), followed by the steps c), d), and e).

[0033] And still in another embodiment of the process as herein disclosed, the processing agent is added after the addition of the water-soluble acid of step b), followed by the steps c), d), and e).

[0034] Preferably, the processing agent is added before and/or during the addition of the water-soluble acid of step b), followed by the steps c), d), and e).

[0035] Said at least one processing agent is selected from the group comprising ferrous sulfate, ferric sulfate, ferrous chloride, ferric chloride, aluminum sulfate, and/or their hydrated forms.

[0036] Without being bound to any theory the inventors believe that the at least one processing agent functions as a coagulating agent promoting the assembly of calcium carbonate containing mineral particles which upon further exposure to the mentioned chemicals in the process provide for the ball-shaped surface modified calcium carbonate containing particles.

[0037] The reaction conditions of the process as herein described take place in an aqueous environment in a temperature range above and including 10°C, such as from about 25°C to about 95°C, preferably in a range from about 30°C to about 80°C, more preferably from about 50°C to about 75°C.

[0038] The processing agent is dosed in one or more steps, preferably in one step to said aqueous calcium carbonate containing mineral slurry before, during or after the addition of the at least one water-soluble acid of step b). The processing agent is added in amounts of up to 8 wt.% based on the dry weight of the slurry. Preferably the processing agent is added in amounts from 0.01 wt.% to about 5 wt.%, more preferably from about 0.05wt.% to about 4 wt.%, still more preferably from about 0.4 wt% to about 3wt.%, based on the dry weight of the slurry.

[0039] In a particular embodiment, the processing agent is aluminum sulfate. In a further particular embodiment, the processing agent is aluminum sulfate in its hydrated form. In preferred embodiment the processing agent is aluminum sulfate hexadecahydrate.

[0040] In still a further embodiment, the content of the aluminum sulfate in the process as herein described is up to 4 wt.% based on the weight of the dry slurry, preferably in the range from about 0.1 wt% to about 2 wt.%, more preferably from about 0.2 wt% to about 1 wt%, based on the dry slurry. It has to be considered that the content of aluminum sulfate is crucial thus dosing of the hydrate requires the corresponding adaption to achieve the desired amount.

[0041] After mixing the slurry can be dewatered in an optional step e), by any type of thermal and/or mechanical methods known to the skilled person.

[0042] The aqueous slurry thus obtained can be further treated such as drying the aqueous slurry in order to obtain a dry surface modified calcium carbonate comprising mineral of spherical or ball-shape. The drying method applied to obtain a dry surface modified calcium carbonate comprising mineral of spherical or ball-shape can be any kind of drying method well known to the skilled person.

[0043] The aqueous ball-shaped surface modified calcium carbonate containing mineral comprised in the slurry obtained by the process of the present invention, has a median grain diameter of from 4 μm to about 100 μm, preferably from about 5 μm to about 75 μm, more preferably from about 10 μm to about 50 μm, still more preferably from about 15 μm to about 30 μm.

[0044] The aqueous ball-shaped surface modified calcium carbonate containing mineral comprised in the slurry obtained by the process of the present invention, has at the same time a narrow particle size distribution d_{98}/d_{50} preferably

smaller than 3, more preferably smaller than 2.5, preferably in a range from 1.4 to 2.9.

[0045] Still further the aqueous surface modified calcium carbonate containing mineral comprised in the slurry obtained by the process herein described, has a BET specific surface area of more than 15 m²/g, and preferably from about 20 m²/g to about 200 m²/g, more preferably from about 30 m²/g to about 150 m²/g, even more preferably from about 40 m²/g to about 100 m²/g.

[0046] A BET specific surface area within the meaning of the present invention relates to the specific surface area measured via the method provided in the examples section hereafter.

[0047] In a preferred embodiment, the aqueous ball-shaped surface modified calcium carbonate containing mineral comprised in the slurry obtained by the process of the present invention, has a BET specific surface area from 30 m²/g to about 90 m²/g and a median grain diameter from 10 µm to 50 µm.

[0048] According to another embodiment, the aqueous slurry of the ball-shaped surface modified calcium carbonate containing mineral obtained by the process as herein described can be further dried to obtain a dry ball-shaped surface modified calcium carbonate containing mineral.

[0049] According to still another embodiment, said dry ball-shaped surface modified calcium carbonate containing mineral, has a BET specific surface area of more than 15 m²/g, and preferably from about 20 m²/g to about 200 m²/g, more preferably from about 30 m²/g to about 150 m²/g, even more preferably from about 40 m²/g to about 100 m²/g. Further said dry ball-shaped surface modified calcium carbonate containing mineral, has a median grain diameter of from 4 µm to about 100 µm, preferably from about 5 µm to about 75 µm, more preferably from about 10 µm to about 50 µm, still more preferably from about 15 µm to about 30 µm.

Fig. 1: shows particle size distribution curves of surface modified calcium carbonate containing minerals according to the present invention

Fig. 2a: shows an SEM picture of ball-shaped surface modified calcium carbonate containing mineral of E2, at 500x magnification.

Fig. 2b: shows an SEM picture of ball-shaped surface modified calcium carbonate containing mineral of E2, at 2500x magnification.

Fig. 3a: shows an SEM picture of ball-shaped surface modified calcium carbonate containing mineral of E6, at 500x magnification.

Fig. 3b: shows an SEM picture of ball-shaped surface modified calcium carbonate containing mineral of E6, at 2500x magnification.

Use of the Invention

[0050] The inventive ball-shaped surface modified calcium carbonate containing mineral or a slurry comprising said inventive ball-shaped surface modified calcium carbonate containing mineral may be used in paper, tissue paper, digital photo paper, paints, coatings, adhesives, plastics, or in waste water treatment or waste water treating agents.

[0051] In preferred embodiment, the inventive ball-shaped surface modified calcium carbonate containing mineral is used in paints or coatings as a matting agent. By matting agent, the applicant understands an agent being capable of scattering the incoming light away from the specular reflectance angle. This means diffracting the directed light that illuminates the substrate causing diffuse scatter.

[0052] In particular the matting agent is present in amounts of 1 to 10 wt.%, preferably in amounts of 2 to 7 wt.%, more preferably in amount of 3 to 5 wt.%, based on the total weight of the paint or coating.

[0053] The paints or coatings comprising the inventive ball-shaped surface modified calcium carbonate containing mineral as matting agents in the amounts mentioned above provide for a surface gloss at 85° in the range of below 10 gloss units (GU), preferably from 0.5 to 9.5, more preferably from 1 to 8, still more preferably from 2 to 6.5, of the dried film of the paint or coating, when measured according to DIN 67 530, which is very surprising due to the low content of the matting agent.

[0054] A further advantage of the inventive ball-shaped surface modified calcium carbonate containing mineral present in amounts as described above is, that besides the matting effect of the dried film of the paint or coating, the surface of said dried paint or coating is smooth.

[0055] Thus, the inventive ball-shaped surface modified calcium carbonate containing mineral of the present invention when used in paints and/or coatings, provide for matt appearance while at the same time providing a haptic smooth surface.

[0056] The following examples are meant to illustrate the invention without restricting its scope:

Measurement Methods

[0057] The following measurement methods are used to evaluate the parameters given in the description, examples

and claims.

BET Specific Surface Area (SSA) of a material

[0058] The specific surface area is measured with nitrogen via the BET method according to ISO 9277 using a Gemini V sold by the company MICROMERITICS™, following conditioning of the sample by heating at 250°C for a period of 30 minutes. Prior to such measurements, the sample is filtered within a Büchner funnel, rinsed with deionised water and dried overnight at 90°C to 100°C in an oven. Subsequently, the dry cake is ground thoroughly in a mortar and the resulting powder placed in a moisture balance at 130°C until a constant weight is reached.

Solids content of an aqueous slurry

[0059] The slurry solids content (also known as "dry weight") is determined using a Moisture Analyser HR73 commercially available from Mettler-Toledo with the following settings: temperature of 120°C, automatic switch off 3, standard drying, 5-20 g of slurry.

Particle size distribution (mass % particles with a diameter < x) and weight median diameter (d₅₀) of non-surface reacted calcium carbonate comprising material (i.e. calcium carbonate starting material)

[0060] Weight median grain diameter and grain diameter mass distribution of a particulate material such as calcium carbonate, are determined via the sedimentation method, i.e. an analysis of sedimentation behavior in a gravimetric field. The measurement is made with a Sedigraph TM 5120.

[0061] The method and instrument are known to the skilled person and are commonly used to determine grain size of fillers and pigments. The measurements is carried out in an aqueous solution of 0.1 wt-% Na₄P₂O₇. The samples were dispersed using a high speed mixer and ultrasound.

Median grain diameter d₅₀ and d₉₈ of ball-shaped surface modified calcium carbonate containing mineral

[0062] Median grain diameter, d₅₀ and d₉₈, of ball-shaped surface modified calcium carbonate containing mineral was determined using a Malvern Mastersizer 2000 Laser Diffraction System, with a defined RI of 1.57 and iRI of 0.005, Malvern Application Software 5.60. The measurement was performed on an aqueous dispersion. The samples were dispersed using a high-speed stirrer. In this respect, the d₅₀ and d₉₈ values define the diameters, at which 50 vol.% or 98 vol.% of the particles measured, have a diameter smaller than d₅₀ or d₉₈ value, respectively.

Viscosity measurements

A. ICI Viscosity according to EN ISO 2884-1

[0063] The ICI viscosity was measured according to EN ISO 2884-1 using a cone-and plate viscometer (Epprecht Instruments + Controls, Bassersdorf, Switzerland) at a shear rate of 10 000 1/s at a temperature of (23 ± 0.2) °C. The measured value after 15 s, which should be a constant value, depicts the measured viscosity of the sample.

B. Viscosity with a Paar Physica M301 PP25 rheometer

[0064] This measurement was conducted with a Paar Physica M301 PP25 Rheometer, from the company Anton Paar GmbH, Austria, according to the following regime: Temp.: 23°C

Starting shear rate: 0.1 1/s

End shear rate: 100 1/s, with a logarithmic gradient of 10 measurement points per decade, and each measurement point taken after 5 seconds.

The measurement points are displayed in a decimal logarithmic manner, so that a linear plot with a negative slope results from this measurement. The x-axis of the graph represents the shear rate in a decimal logarithmic manner, and the y-axis depicts the measured viscosity in Pa·s.

Gloss of a coated surface

[0065] The Gloss values are measured at the listed angles according to DIN 67 530 on painted surfaces prepared with a coater gap of 150 µm and 300 µm on contrast cards. The contrast cards used are Leneta contrast cards, form 3-B-H, size 7-5/8 x 11-3/8 (194 x 289 mm), sold by the company Leneta, and distributed by Novamart, Stäfa, Switzerland.

The gloss is measured with a gloss measurement device from the company Byk Gardner, Geretsried, Germany. The gloss is obtained by measuring 5 different points on the card with the gloss measurement device, and the average value is calculated by the device and can be derived from the display of the device.

5 Scrubbing test

[0066] For the scrubbing test, Laneta contrast cards, form 3-B-H, size 7-5/8 x 11-3/8 (194 x 289 mm), sold by the company Leneta, and distributed by Novamart, Stäfa, Switzerland, coated with a coater gap of 300 µm, as mentioned above were submitted to a scrubbing test. The scrubbing was performed with a square felt-glider 22 mm x 22 mm fixed on the scrubbing device. The arm holding the felt-glider was loaded with a 500g weight pressing the felt-glider onto the surface of the coated Leneta card. The scrubbing path length was 5cm and 50 cycles (1 cyle = forth and back) where performed within 60 sec ± 2 sec. The felt-glider was of the fix-o-moll type, provided by from Wilhelm Ritterath GmbH, Meckenheim, Germany. Gloss was measured according to DIN 67 530 at 60° and 85° before and after scrubbing.

15 Determination of colour values (R_x , R_y , R_z)

[0067] The colour values R_x , R_y , R_z are determined over the white and black fields of the Leneta contrast card, and are measured with a spectraflas SF 450 X spectrophotometer of the company Datacolor, Montreuil, France.

20 Contrast Ratio (opacity) of a coated surface

[0068] Contrast ratio values are determined according to ISO 2814 at a spreading rate of 7.5 m²/l.

[0069] The contrast ratio is calculated as described by the equation below:

$$25 \quad \text{Contrast ratio } [\%] = \frac{R_{y \text{ black}}}{R_{y \text{ white}}} \times 100 \%$$

30 with $R_{y \text{ black}}$ and $R_{y \text{ white}}$ being obtained by the measurement of the color values.

Examples

35 [0070] The following illustrative examples of the invention involve contacting a calcium carbonate containing mineral, namely a ground natural marble according to the process of the present invention in a jacketed steel reactor equipped with a laminar mixing system in a batch size of 10 l. The solid content is adjusted to either 10 wt.% or 8 wt.% solids, as indicated in table 1.

[0071] The addition of the at least one water-soluble acid of step b) and the contacting of said aqueous calcium carbonate containing mineral slurry of step a) with said acid of step b) and with said CO₂ generated in situ and/or supplied externally of step d) take place in a stirred reactor under stirring conditions such as to develop an essentially laminar flow.

40 [0072] The marble used in the process of the present invention and indicated as H90 in table 1., is a commercially available product from the applicant sold under the brand name Hydrocarb® 90-ME 78%, which is a natural ground marble from Molde in Norway, having a top cut d_{98} of 5 µm, and weight median particle size d_{50} of 0.7 µm (size determined by Sedigraph), and provided in form of a slurry with solids content of 78 wt.% based on dry matter of the slurry and a viscosity of 400 mPas.

45 [0073] The mixing speed is adjusted to either 140 or 300 rpm, and the temperature is adjusted to 70°C. Prior to the dosing of a 30 wt.% of phosphoric acid solution, which is added over a period of 10 or 30 min, the processing agent aluminum sulfate hexadecahydrate was added at once to the calcium carbonate containing mineral slurry in amounts of 0.5 wt.% or 0.6 wt.%.

50 [0074] The reaction was mixed at the indicated mixing speeds and times according to table 1.

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Table 1.

	Tank Conditions					H ₃ PO ₄ 30 wt. %		Al ₂ (SO ₄) ₃ *16H ₂ O	
	Batch Size (l)	Mixing Speed (rpm)	Target Slurry Solids wt. %	Feed Slurry Type	Temp. °C	dosing of wt. %	Added over a period of	Final conc. wt. %	Addition time
E1	10.00	300	10.0	H90	70	30.0	10 min	0.5	b/a
E2	10.00	300	8.0	H90	70	30.0	10 min	0.5	b/a
E3	10.00	300	10.0	H90	70	30.0	10 min	0.6	b/a
E4	10.00	140	10.0	H90	70	30.0	10 min	0.5	b/a
E5	10.00	140	8.0	H90	70	30.0	10 min	0.5	b/a
E6	10.00	140	10.0	H90	70	30.0	30 min	0.5	b/a
E7	10.00	140	10.0	H90	70	30.0	10 min	0.6	b/a
b/a means addition before acid									

[0075] The particle size distribution (PSD) of examples E1 to E7 were measured on a Malvern Mastersizer and the particle size distribution curves are shown in Fig. 1. Table 2 provides for the BET specific surface area SSA, the top cut d_{98} and the median grain diameter d_{50} for the examples E1 to E7.

Table 2.

		E1	E1	E3	E4	E5	E6	E7
SSA	m ² /g	53.9	62.5	56.7	62.2	56.9	57.8	59.6
d_{50}^*	μm	19.7	27.9	18.9	34.5	30.4	15.3	22.8
d_{98}^*	μm	41.6	46.6	38.3	57.8	50.7	27.3	39.3
d_{98}/d_{50}		2.1	1.7	2.1	1.7	1.7	1.8	1.7
* determined by Malvern Mastersizer								

[0076] The examples E2, E6, and E7 of surface modified calcium carbonates were tested in paints. For this, E2, E6 and E7 were mixed in formulations and compared with matting agents used in this area such as diatomaceous earths (C1, C3) or aluminum silicate (C2). The dosage level of all matting agents was at 3wt. %. Said formulations further comprise common additives such as defoamers, dispersing agents, sodium hydroxide, fungicides, bactericides, titanium dioxide (rutile), talcum, fillers, pigments, thickeners, plasticizer, viscosity modifiers, water, and others known to the skilled person. Table 3 provides for the composition of the test paint.

Table 3.

Base test paint		C1	C2	C3	P2	P6	P7
Water	g	331	331	331	331	331	331
Calgon N neu	g	1	1	1	1	1	1
Bermocoll EHM 200	g	3	3	3	3	3	3
Sodium hydroxide, 10 %	g	2	2	2	2	2	2
BYK 038	g	3	3	3	3	3	3
ECODIS P 50	g	3	3	3	3	3	3
Mergal 723K	g	2	2	2	2	2	2
Tiona 595	g	60	60	60	60	60	60
Finntalc M20SL - AW	g	80	80	80	80	80	80

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(continued)

Base test paint			C1	C2	C3	P2	P6	P7
5	Omyacarb EXTRA - CL	g	150	150	150	150	150	150
	Omyacarb 2 - GU	g	220	220	220	220	220	220
	Mowilith LDM 6119, 50%	g	115	115	115	115	115	115
	Matting agents							
10	Celite 281 (Diatomaceous Earth)	g	30					
	OpTiMat 2550 (Aluminum Silicate)	g		30				
	Celatom MW 27 (Diatomaceous Earth)	g			30			
15	E2	g				30		
	E6	g					30	
	E7							30
20	COAPUR 4435* (Polyurethan thickener)	g	10	10	10	10	10	10
	Total	g	1 010	1 010	1 010	1 010	1 010	1 010
*the 1% of COAPUR 4435 was added after the paint production to raise the viscosity to an applicable level.								

[0077] The fillers and pigments were replaced on a volume basis, i.e. at identical Pigment Volume Concentration (PVC). The paints were tested for dry opacity (ISO 2814), whiteness R_y (DIN 53145) and sheen (DIN67530) (gloss at 85°). The components and functions of the materials for the base test paint are commercially available products known to the skilled person and listed in table 4 hereto below.

Table 4 - Material for base paint.

Base test paint	Producer	Chemical basis	Function
Water	In house, deionized	H ₂ O	Solvent
35 Calgon N new	BK Giulini Chemie	Sodium polyphosphate	Wetting and dispersing agent
Bermocoll EHM 200	AkzoNobel Corp.	Ethyl Hydroxyethyl cellulose	Thickener
40 Sodium hydroxide, 10 %	Various	NaOH solution	pH regulator
BYK 038	Byk Chemie	Mineral oil basis	Defoamer
ECODIS P 50	Coatex SA	Sodium salt of acrylic polymer	Wetting and dispersing agent
45 Mergal 723K	Troy Chemie GmbH	Benzisothiazolone basis, without formaldehyde	Preservative
Tiona 595	Millenium Inorganic Chemicals	Titanium dioxide, rutile (Al,org. coated)	White pigment
50 Finntalc M20SL - AW	Mondo Minerals	Magnesium Silicate	Extender
Omyacarb EXTRA - CL	Omya Clariana SA	Calcium carbonate, marble	Extender
55 Omyacarb 2 - GU	Omya	Calcium carboanate, marble	Extender

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(continued)

Base test paint	Producer	Chemical basis	Function
Mowilith LDM 6119, 50%	Clariant	non-plasticized aqueous polymer dispersion based on styrene and an acrylic acid ester	Binder (copolymer)
Matting agents			
Celite 281 (Diatomaceous Earth)	Celite France	Diatomaceous Earth (silica)	Matting agent
OpTiMat 2550	Imerys	Aluminum silicate	Matting agent
Celatom MW 27	EP Minerals	Diatomaceous Earth	Matting agent
E2	Omya	Surface modified marble	Matting agent
E6	Omya	Surface modified marble	Matting agent
Paint thickener	Various Producers	Polyurethane	Thickener

[0078] The performance of the tested paints is summarized in table 5, wherein C1, C2, and C3 refer to comparative paint examples and P2, P6, and P7 refer to the paint examples comprising the surface modified calcium carbonate containing minerals obtained by the process of the present invention.

Table 5. Performance of paints

		C1	C2	C3	P2	P6	P7
Temperature	°C	23	23	23	23	23	23
ICI Viscosity		180	170	160	200	200	200
Paar Physica Viscosity							
Viscosity, $\gamma=1 \text{ s}^{-1}$	Pas	16 800	19 000	18 700	22 500	24 100	24 600
Viscosity, $\gamma=5 \text{ s}^{-1}$	Pas	6 450	7 130	7 010	8 940	9680	9 240
Viscosity, $\gamma=10 \text{ s}^{-1}$	Pas	4 380	4 790	4 700	6150	6 640	6190
Viscosity, $\gamma=40 \text{ s}^{-1}$	Pas	2080	2270	2 160	2860	360	2710
Optical properties 150 micrometer, 300 micrometers and 7.5 m² / l							
150 micrometer							
Ry	%	90.4	89.8	90.2	90.9	91.0	91.1
Ry over black	%	87.9	87.4	88.0	89.1	89.1	89.4
Yellowness Index		2.5	2.6	2.5	2.0	2.0	2.1
Contrast Ratio	%	97.2	97.4	97.5	98.0	98.0	98.2
Gloss 85°		4.9	2.9	3.9	3.6	5.6	3.6
300 micrometer							
Ry	%	90.9	90.2	90.8	91.6	91.7	91.8
Ry over black	%	90.3	89.7	90.3	91.2	91.3	91.3
Yellowness Index		2.7	2.8	2.7	2.3	2.3	2.4
Contrast Ratio	%	99.3	99.4	99.4	99.5	99.5	99.5
Gloss 85°		5.0	3.3	4.5	4.4	6.2	4.1

(continued)

Opacity at 7.5 m ² /l							
Contrast ratio	%	98.1	98.1	98.1	98.8	98.8	98.9
Polishing CROWN 300μ							
Gloss 60° unscrub		2.7	2.6	2.6	2.7	2.7	2.7
Gloss 60° scrub		5.7	5.9	5.6	6.6	6.5	6.5
Gloss 85° unscmb		5.4	3.1	4.6	4.2	6.2	4.2
Gloss 85° scrub		29.5	18.7	27.1	31.7	36.3	29.5

[0079] As can be seen from the results of table 4, the examples of the present invention show a performance in matting effect similar to matting agents of the prior art. Such matting effects have up to now not been observed for paints comprising the surface modified calcium carbonate containing minerals having a median grain diameter from about 10 μm to about 50 μm, and having a BET specific surface area from about 30 m²/g to about 90 m²/g of the present invention. The paint properties were measured for dry opacity at 150 μm and 300 μm film thickness, and the contrast ratio was determined at 7.5 m²/l. P2, P6, and P7 provide for a gloss at 85° of 4.1, 6.2, and 4.1 at a coating thickness of 300 μm. This is also in expectation of the matting effect to decrease with decreasing particle size.

[0080] Therefore, the present invention provides for alternative matting agents based on calcium carbonate containing mineral, providing a matting effect when used in paints and/or coatings, while at the same time providing a haptic smooth surface. Further to this, the present invention provides for a process for obtaining such surface modified calcium carbonate containing minerals, wherein said surface modified calcium carbonate containing minerals can be used in paper and paper coating, tissue paper, digital photo paper, paints, coatings, adhesives, plastics, or in waste water treating agents.

Claims

1. Process for producing ball-shaped spherical surface modified calcium carbonate comprising particles comprising the steps of:
 - a) providing at least one aqueous calcium carbonate containing mineral slurry;
 - b) providing at least one water-soluble acid;
 - c) optionally providing further gaseous CO₂ via an external route;
 - d) contacting said aqueous calcium carbonate containing mineral slurry of step a) with said acid of step b) and with said CO₂ generated in situ and/or supplied externally of step c) under stirring conditions,
 - e) optionally dewatering the aqueous slurry;

wherein at least one processing agent is added before, during or after said aqueous calcium carbonate containing mineral slurry of step a) is contacted with said acid of step b) and with said CO₂ generated in situ and/or supplied externally of step c), and

wherein the at least one processing agent is selected from the group consisting of ferrous sulfate, ferric sulfate, ferrous chloride, ferric chloride, aluminum sulfate, and/or their hydrated forms, and

wherein the processing agent is added in amounts of up to 8 wt.% based on the dry weight of the slurry.
2. Process according to claim 1, wherein said calcium carbonate containing mineral is selected from the group consisting of marble, chalk, limestone, calcite, dolomite, precipitated calcium carbonate (PCC), and mixtures thereof.
3. Process according to claim 1 or 2, wherein said calcium carbonate containing mineral in the slurry has a weight median particle diameter of 0.01 μm to 10 μm, preferably from 0.2 μm to 2 μm, more preferably from 0.5 μm to 1 μm.
4. Process according to one of claims 1 to 3, wherein said slurry of step a) has a solids content of greater than 4 wt.-%, preferably from 5 wt.-% to about 20 wt.-%, based on the weight of the slurry.
5. Process according to one of claims 1 to 4, wherein said slurry of step a) is stabilized by the addition of one or more dispersants.

6. Process according to one of the claims 1 to 5, wherein the at least one water-soluble acid of step b) has a pK_a from 0 to 6, preferably has a pK_a from 0 to 2.5.
- 5 7. Process according to one of the claims 1 to 6, wherein the at least one water-soluble acid of step b) is selected from phosphoric acid, citric acid, boric acid, or mixtures thereof.
8. Process according to one of the claims 1 to 7, wherein the at least one water-soluble acid is dosed in a molar amount relative to the numbers of moles of the calcium carbonate containing mineral in the range from 0.01 mol/mol to about 1 mol/mol, preferably from 0.1 to 0.6 mol/mol.
- 10 9. Process according to one of the claims 1 to 8, wherein the at least one water-soluble acid provided in step b) is added in one or more steps, preferably in one step to said aqueous calcium carbonate containing mineral slurry.
- 15 10. Process according to one of claims 1 to 9, wherein the addition of the at least one water-soluble acid of step b) and the contacting of said aqueous calcium carbonate containing mineral slurry of step a) with said acid of step b) and with said CO_2 generated in situ and/or supplied externally of step c) take place in a stirred reactor under stirring conditions such as to develop an essentially laminar flow.
- 20 11. Process according to one of claims 1 to 10, wherein the process takes place in an aqueous environments in a temperature range above and including $20^\circ C$, such as from about $25^\circ C$ to about $95^\circ C$, preferably in a range from about $30^\circ C$ to about $80^\circ C$, more preferably from about $50^\circ C$ to about $75^\circ C$.
- 25 12. Process according to one of claims 1 to 11, wherein the processing agent is added in amounts from 0.01 wt.% to about 5 wt.%, more preferably from about 0.05 wt.% to about 4 wt.%, still more preferably from about 0.4 wt.% to about 3 wt.%, based on the dry weight of the slurry.
- 30 13. Process according to claims 1 to 12, wherein the processing agent, preferably aluminum sulfate or its hydrate, more preferably aluminum sulfate hexadecahydrate is dosed in one or more steps, preferably in one step to said aqueous calcium carbonate containing mineral slurry.
- 35 14. Process according to claim 13, wherein the content of aluminum sulfate is up to 5 wt.% based on the weight of the dry slurry.
15. Process according to one of claims 1 to 14, wherein the processing agent is added before, during or after step b).
- 40 16. Aqueous slurry of ball-shaped surface modified calcium carbonate containing mineral obtained according to any process of claims 1 to 15, wherein said surface modified calcium carbonate containing mineral has a BET specific surface area of more than $15\text{ m}^2/\text{g}$.
- 45 17. Aqueous slurry according to claim 16, wherein said surface modified calcium carbonate containing mineral has a median grain diameter of from $4\text{ }\mu\text{m}$ to about $100\text{ }\mu\text{m}$, preferably from about $5\text{ }\mu\text{m}$ to about $75\text{ }\mu\text{m}$, more preferably from about $10\text{ }\mu\text{m}$ to about $50\text{ }\mu\text{m}$, still more preferably from about $15\text{ }\mu\text{m}$ to about $30\text{ }\mu\text{m}$, determined by Malvern Mastersizer.
- 50 18. Aqueous slurry according to one of claims 16 or 17, wherein said surface modified calcium carbonate containing mineral has a BET specific surface area from about $20\text{ m}^2/\text{g}$ to about $200\text{ m}^2/\text{g}$, preferably from about $30\text{ m}^2/\text{g}$ to about $150\text{ m}^2/\text{g}$, more preferably from about $40\text{ m}^2/\text{g}$ to about $100\text{ m}^2/\text{g}$.
- 55 19. Aqueous slurry according to claim 18, wherein said surface modified calcium carbonate containing mineral has a BET specific surface area from $30\text{ m}^2/\text{g}$ to about $90\text{ m}^2/\text{g}$ and a median grain diameter from $10\text{ }\mu\text{m}$ to $50\text{ }\mu\text{m}$, determined by Malvern Mastersizer.
20. Aqueous slurry according to one of claims 16 to 19, wherein the ball-shaped surface modified calcium carbonate comprising mineral has a narrow particle size distribution d_{98}/d_{50} preferably smaller than 3, more preferably smaller than 2.5, preferably in a range from 1.4 to 2.9.
21. Surface modified calcium carbonate containing mineral obtained by drying the aqueous slurry of any one of claims 16 to 20, wherein said surface modified calcium carbonate containing mineral has a BET specific surface area of

more than 15 m²/g.

22. Surface modified calcium carbonate containing mineral of claim 21, wherein the surface modified calcium carbonate containing mineral has a BET specific surface area from about 20 m²/g to about 200 m²/g, preferably from about 30 m²/g to about 150 m²/g, more preferably from about 40 m²/g to about 100 m²/g.
23. Surface modified calcium carbonate containing mineral of claim 21, wherein the surface modified calcium carbonate containing mineral has a median grain diameter of from 4 μm to about 100 μm, preferably from about 5 μm to about 75 μm, more preferably from about 10 μm to about 50 μm, still more preferably from about 15 μm to about 30 μm, determined by Malvern Mastersizer.
24. Surface modified calcium carbonate containing mineral of claim 21, wherein the surface modified calcium carbonate containing mineral has a BET specific surface area from 30 m²/g to about 90 m²/g and a median grain diameter from 10 μm to 50 μm, determined by Malvern Mastersizer.
25. Use of the surface modified calcium carbonate containing mineral of the aqueous slurry of any of claims 16 to 20, or the dry ball-shaped surface modified calcium carbonate containing mineral of claim 21 to 24, in paper, paper coating, tissue paper, digital photo paper, paints, coatings, adhesives, plastics, waste water treating or waste water treating agents.
26. Use according to claim 25 as matting agent in paints and coatings.
27. Use according to claim 26, wherein the matting agent is present in amounts of 1 to 10 wt.%, preferably of 2 to 7 wt.%, more preferably of 3 to 5 wt.% based on the wet paint.
28. Use according to claim 27, wherein surface of the dried paint or coating has a gloss at 85° in the range of below 10, preferably from 0.5- 9.5, more preferably from 1 to 8, still more preferably from 2-6.5, when measured according to DIN 67 530.
29. Paper, tissue paper, digital photo paper, paints, coatings, adhesives, plastics, or waste water treating agent comprising the ball-shaped surface modified calcium carbonate containing mineral of the aqueous slurry of any of claims 16 to 20, or the dry ball-shaped surface modified calcium carbonate containing mineral of claim 21 to 24.

Patentansprüche

1. Verfahren zur Herstellung von ballförmigen kugelförmigen oberflächenmodifiziertes Calciumcarbonat umfassenden Partikeln, umfassend die Schritte:
 - a) Bereitstellen von wenigstens einer wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung;
 - b) Bereitstellen von wenigstens einer wasserlöslichen Säure;
 - c) gegebenenfalls Bereitstellen von weiterem gasförmigem CO₂ über eine externe Route;
 - d) Inkontaktbringen der wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung aus Schritt a) mit der Säure aus Schritt b) und mit dem CO₂, erzeugt in situ und/oder extern zugeführt aus Schritt c), unter Rührbedingungen,
 - e) gegebenenfalls Entwässern der wässrigen Aufschlämmung;wobei wenigstens ein Verarbeitungsmittel vor, während oder nach der wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung aus Schritt a) mit der Säure aus Schritt b) und mit dem CO₂, erzeugt in situ und/oder extern zugeführt aus Schritt c), in Kontakt gebracht wird, und wobei das wenigstens eine Verarbeitungsmittel ausgewählt ist aus der Gruppe bestehend aus Eisen(II)-sulfat, Eisen(III)-sulfat, Eisen(II)-chlorid, Eisen(III)-chlorid, Aluminiumsulfat und/oder ihren hydratisierten Formen, und wobei das Verarbeitungsmittel in Mengen von bis zu 8 Gew.-%, bezogen auf das Trockengewicht der Aufschlämmung, zugegeben wird.
2. Verfahren nach Anspruch 1, bei dem das Calciumcarbonat enthaltende Mineral ausgewählt ist aus der Gruppe bestehend aus Marmor, Kreide, Kalkstein, Calcit, Dolomit, gefälltem Calciumcarbonat (PCC), sowie Gemischen davon.

3. Verfahren nach Anspruch 1 oder 2, bei dem das Calciumcarbonat enthaltende Mineral in der Aufschlämmung einen gewichtsgemittelten Partikeldurchmesser von 0,01 μm bis 10 μm aufweist, bevorzugt von 0,2 μm bis 2 μm , bevorzugter von 0,5 μm bis 1 μm .
- 5 4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem die Aufschlämmung aus Schritt a) einen Feststoffgehalt von größer 4 Gew.-% aufweist, bevorzugt von 5 Gew.-% bis etwa 20 Gew.-%, bezogen auf das Gewicht der Aufschlämmung.
- 10 5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem die Aufschlämmung aus Schritt a) durch die Zugabe von einem oder mehreren Dispergierungsmitteln stabilisiert wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem die wenigstens eine wasserlösliche Säure aus Schritt b) einen pK_a von 0 bis 6 aufweist, bevorzugt von 0 bis 2,5.
- 15 7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem die wenigstens eine wasserlösliche Säure aus Schritt b) ausgewählt ist aus Phosphorsäure, Zitronensäure, Borsäure oder Gemischen davon.
8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die wenigstens eine wasserlösliche Säure in einer molaren Menge, bezogen auf die Anzahl an Mol des Calciumcarbonat enthaltenden Minerals, im Bereich von 0,01 Mol/Mol bis etwa 1 Mol/Mol dosiert wird, bevorzugt von 0,1 bis 0,6 Mol/Mol.
- 20 9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem die wenigstens eine wasserlösliche Säure, die in Schritt b) bereitgestellt wird, in einem oder mehreren Schritten zugegeben wird, bevorzugt in einem Schritt zu der wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung.
- 25 10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem die Zugabe der wenigstens einen wasserlöslichen Säure aus Schritt b) und das Inkontaktbringen der wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung aus Schritt a) mit der Säure aus Schritt b) und mit dem CO_2 , erzeugt in situ und/oder extern zugeführt aus Schritt c), in einem gerührten Reaktor unter Rührbedingungen stattfindet, so dass sich eine im wesentlichen laminare Strömung entwickelt.
- 30 11. Verfahren nach einem der Ansprüche 1 bis 10, bei dem das Verfahren in einer wässrigen Umgebung bei einem Temperaturbereich oberhalb und einschließlich 20°C stattfindet, wie von etwa 25°C bis etwa 95°C, bevorzugt im Bereich von etwa 30°C bis etwa 80°C, bevorzugter von etwa 50°C bis etwa 75°C.
- 35 12. Verfahren nach einem der Ansprüche 1 bis 11, bei dem das Verarbeitungsmittel in Mengen von 0,01 Gew.-% bis etwa 5 Gew.-% zugegeben wird, bevorzugter von etwa 0,05 Gew.-% bis etwa 4 Gew.-%, noch bevorzugter von etwa 0,4 Gew.-% bis etwa 3 Gew.-%, bezogen auf das Trockengewicht der Aufschlämmung.
- 40 13. Verfahren nach Anspruch 1 bis 12, bei dem das Verarbeitungsmittel, bevorzugt Aluminiumsulfat oder sein Hydrat, bevorzugter Aluminiumsulfat-Hexahydrat, in einem oder mehreren Schritten dosiert wird, bevorzugt in einem Schritt zu der wässrigen Calciumcarbonat enthaltenden Mineralaufschlämmung.
- 45 14. Verfahren nach Anspruch 13, bei dem der Gehalt an Aluminiumsulfat bis zu 5 Gew.-% beträgt, bezogen auf das Gewicht der trockenen Aufschlämmung.
15. Verfahren nach einem der Ansprüche 1 bis 14, bei dem das Verarbeitungsmittel vor, während oder nach Schritt b) zugegeben wird.
- 50 16. Wässrige Aufschlämmung von ballförmigem oberflächenmodifiziertem Calciumcarbonat enthaltendem Mineral, erhalten gemäß einem Verfahren der Ansprüche 1 bis 15, bei dem das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von mehr als 15 m^2/g aufweist.
- 55 17. Wässrige Aufschlämmung nach Anspruch 16, bei der das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral einen mittleren Korndurchmesser von 4 μm bis etwa 100 μm aufweist, bevorzugt von etwa 5 μm bis etwa 75 μm , bevorzugter von etwa 10 μm bis etwa 50 μm , noch bevorzugter von etwa 15 μm bis etwa 30 μm , bestimmt durch Malvern Mastersizer.

18. Wässrige Aufschlämmung nach einem der Ansprüche 16 oder 17, bei der das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von etwa 20 m²/g bis etwa 200 m²/g aufweist, bevorzugt von etwa 30 m²/g bis etwa 150 m²/g, bevorzugter von etwa 40 m²/g bis etwa 100 m²/g.
- 5 19. Wässrige Aufschlämmung nach Anspruch 18, bei der das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von 30 m²/g bis etwa 90 m²/g aufweist, und einen mittleren Korndurchmesser von 10 µm bis 50 µm, bestimmt durch Malvern Mastersizer.
- 10 20. Wässrige Aufschlämmung nach einem der Ansprüche 16 bis 19, bei der das ballförmige oberflächenmodifizierte Calciumcarbonat umfassende Mineral eine enge Partikelgrößenverteilung d_{98}/d_{50} von bevorzugt kleiner 3 aufweist, bevorzugter kleiner 2,5, bevorzugt in einem Bereich von 1,4 bis 2,9.
- 15 21. Oberflächenmodifiziertes Calciumcarbonat enthaltendes Mineral, erhalten durch Trocknen der wässrigen Aufschlämmung gemäß einem der Ansprüche 16 bis 20, bei dem das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von mehr als 15 m²/g aufweist.
- 20 22. Oberflächenmodifiziertes Calciumcarbonat enthaltendes Mineral von Anspruch 21, bei dem das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von etwa 20 m²/g bis etwa 200 m²/g aufweist, bevorzugt von etwa 30 m²/g bis etwa 150 m²/g, bevorzugter von etwa 40 m²/g bis etwa 100 m²/g.
- 25 23. Oberflächenmodifiziertes Calciumcarbonat enthaltendes Mineral von Anspruch 21, bei dem das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral einen mittleren Korndurchmesser von 4 µm bis etwa 100 µm aufweist, bevorzugt von etwa 5 µm bis etwa 75 µm, bevorzugter von etwa 10 µm bis etwa 50 µm, noch bevorzugter von etwa 15 µm bis etwa 30 µm, bestimmt durch Malvern Mastersizer.
- 30 24. Oberflächenmodifiziertes Calciumcarbonat enthaltendes Mineral von Anspruch 21, bei dem das oberflächenmodifizierte Calciumcarbonat enthaltende Mineral eine BET spezifische Oberfläche von 30 m²/g bis etwa 90 m²/g aufweist, und einen mittleren Korndurchmesser von 10 µm bis 50 µm, bestimmt durch Malvern Mastersizer.
- 35 25. Verwendung des oberflächenmodifizierten Calciumcarbonat enthaltenden Minerals der wässrigen Aufschlämmung gemäß einem der Ansprüche 16 bis 20, oder des trockenen ballförmigen oberflächenmodifizierten Calciumcarbonat enthaltenden Minerals von Anspruch 21 bis 24 in Papier, Papierbeschichtung, Tissue-Papier, Digitalfotopapier, Farben, Beschichtungen, Klebstoffen, Kunststoffen, Abwasserbehandlung oder Abwasserbehandlungsmitteln.
- 40 26. Verwendung nach Anspruch 25 als Mattierungsmittel in Farben und Beschichtungen.
27. Verwendung nach Anspruch 26, bei der das Mattierungsmittel in Mengen von 1 bis 10 Gew.-% anwesend ist, bevorzugt von 2 bis 7 Gew.-%, bevorzugter von 3 bis 5 Gew.-%, bezogen auf die nasse Farbe.
- 45 28. Verwendung nach Anspruch 27, bei der die Oberfläche der trockenen Farbe oder Beschichtung einen Glanz bei 85° im Bereich von unter 10 aufweist, bevorzugt von 0,5 - 9,5, bevorzugter von 1 bis 8, noch bevorzugter von 2 - 6,5, wenn gemäss DIN 67 530 gemessen.
29. Papier, Tissue-Papier, Digitalfotopapier, Farben, Beschichtungen, Klebstoffe, Kunststoffe oder Abwasserbehandlungsmittel, umfassend ballförmiges oberflächenmodifiziertes Calciumcarbonat enthaltendes Mineral der wässrigen Aufschlämmung gemäß einem der Ansprüche 16 bis 20, oder das trockene ballförmige oberflächenmodifizierte Calciumcarbonat enthaltende Mineral von Anspruch 21 bis 24.

50 Revendications

1. Procédé de production de particules sphériques en forme de billes comprenant du carbonate de calcium modifié en surface comprenant les étapes consistants à :
- 55 a) fournir au moins une suspension aqueuse de substance minérale contenant du carbonate de calcium ;
b) fournir au moins un acide soluble dans l'eau ;
c) fournir facultativement davantage de CO₂ gazeux par le biais d'une voie externe ;
d) mettre en contact ladite suspension aqueuse de substance minérale contenant du carbonate de calcium de

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l'étape a) avec ledit acide de l'étape b) et avec ledit CO_2 produit in situ et/ou fourni de manière externe de l'étape c) dans des conditions d'agitation,
e) facultativement déshydrater la suspension aqueuse ;

- 5 dans lequel au moins un adjuvant est ajouté avant, pendant ou après la mise en contact de ladite suspension aqueuse de substance minérale contenant du carbonate de calcium de l'étape a) avec ledit acide de l'étape b) et avec ledit CO_2 produit in situ et/ou fourni de manière externe de l'étape c), et dans lequel l'adjuvant est choisi dans le groupe constitué par le sulfate ferreux, le sulfate ferrique, le chlorure ferreux, le chlorure ferrique, le sulfate d'aluminium et/ou leurs formes hydratées, et
- 10 dans lequel l'adjuvant est ajouté en des quantités allant jusqu'à 8 % en poids, sur la base du poids sec de la suspension.
2. Procédé selon la revendication 1, dans lequel ladite substance minérale contenant du carbonate de calcium est choisie dans le groupe constitué par le marbre, la craie, le calcaire, la calcite, la dolomite, le carbonate de calcium précipité (CCP) et leurs mélanges.
- 15 3. Procédé selon la revendication 1 ou 2, dans lequel ladite substance minérale contenant du carbonate de calcium a un diamètre de particule médian en poids de $0,01\ \mu\text{m}$ à $10\ \mu\text{m}$, de préférence de $0,2\ \mu\text{m}$ à $2\ \mu\text{m}$, plus préférablement de $0,5\ \mu\text{m}$ à $1\ \mu\text{m}$.
- 20 4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite suspension de l'étape a) a une teneur en matières solides supérieure à 4 % en poids, de préférence de 5 % en poids à environ 20 % en poids, sur la base du poids de la suspension.
- 25 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ladite suspension de l'étape a) est stabilisée par l'ajout d'un ou plusieurs dispersants.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'acide soluble dans l'eau de l'étape b) a un pK_a de 0 à 6, de préférence a un pK_a de 0 à 2,5.
- 30 7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'acide soluble dans l'eau de l'étape b) est choisi parmi l'acide phosphorique, l'acide citrique, l'acide borique ou leurs mélanges.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'acide soluble dans l'eau est ajouté en une quantité molaire par rapport aux nombres de moles de la substance minérale contenant du carbonate de calcium de $0,01\ \text{mol/mol}$ à environ $1\ \text{mol/mol}$, de préférence de $0,1$ à $0,6\ \text{mol/mol}$.
- 35 9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel l'acide soluble dans l'eau fourni dans l'étape b) est ajouté en une ou plusieurs étapes, de préférence en une étape, à ladite suspension aqueuse de substance minérale contenant du carbonate de calcium.
- 40 10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel l'ajout de l'acide soluble dans l'eau de l'étape b) et la mise en contact de la suspension aqueuse de substance minérale contenant du carbonate de calcium de l'étape a) avec ledit acide de l'étape b) et avec ledit CO_2 produit in situ et/ou fourni de manière externe de l'étape c) se produisent dans un réacteur agité dans des conditions d'agitation permettant de développer un flux essentiellement laminaire.
- 45 11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel le procédé a lieu dans un environnement aqueux dans une plage de température au-dessus de et incluant $20\ ^\circ\text{C}$, telle que d'environ $25\ ^\circ\text{C}$ à environ $95\ ^\circ\text{C}$, de préférence dans une plage d'environ $30\ ^\circ\text{C}$ à environ $80\ ^\circ\text{C}$, plus préférablement d'environ $50\ ^\circ\text{C}$ à environ $75\ ^\circ\text{C}$.
- 50 12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'adjuvant est ajouté en des quantités de 0,01 % en poids à environ 5 % en poids, plus préférablement d'environ 0,05 % en poids à environ 4 % en poids, encore plus préférablement d'environ 0,4 % en poids à environ 3 % en poids, sur la base du poids sec de la suspension.
- 55 13. Procédé selon les revendications 1 à 12, dans lequel l'adjuvant, de préférence le sulfate d'aluminium ou son hydrate, plus préférablement le sulfate d'aluminium hexadécahydrate, est ajouté en une ou plusieurs étapes, de préférence

en une étape, à ladite suspension aqueuse de substance minérale contenant du carbonate de calcium.

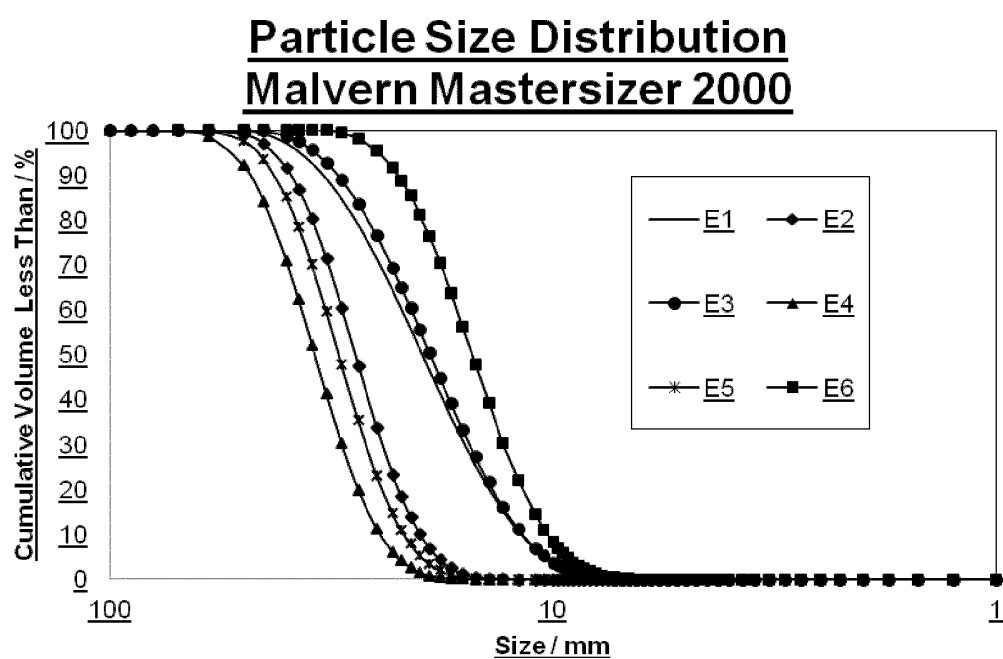
14. Procédé selon la revendication 13, dans lequel la teneur en sulfate d'aluminium est inférieure ou égale à 5 % en poids, sur la base du poids sec de la suspension.
15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel l'adjuvant est ajouté avant, pendant ou après l'étape b).
16. Suspension aqueuse d'une substance minérale en forme de billes contenant du carbonate de calcium modifié en surface obtenue selon l'une quelconque des revendications 1 à 15, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET supérieure à 15 m²/g.
17. Suspension aqueuse selon la revendication 16, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a un diamètre de grain médian de 4 µm à environ 100 µm, de préférence d'environ 5 µm à environ 75 µm, plus préférablement d'environ 10 µm à environ 50 µm, encore plus préférablement d'environ 15 µm à environ 30 µm, déterminé par un appareil Mastersizer de Malvern.
18. Suspension aqueuse selon la revendication 16 ou 17, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET d'environ 20 m²/g à environ 200 m²/g, de préférence d'environ 30 m²/g à environ 150 m²/g, plus préférablement d'environ 40 m²/g à environ 100 m²/g.
19. Suspension aqueuse selon la revendication 18, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET de 30 m²/g à environ 90 m²/g et un diamètre de grain médian de 10 µm à 50 µm, déterminé par un appareil Mastersizer de Malvern.
20. Suspension aqueuse selon l'une quelconque des revendications 16 à 19, dans laquelle la substance minérale en forme de billes contenant du carbonate de calcium modifié en surface a une distribution de taille de particule étroite d₉₈/d₅₀ de préférence inférieure à 3, plus préférablement inférieure à 2,5, de préférence dans la plage de 1,4 à 2,9.
21. Substance minérale contenant du carbonate de calcium modifié en surface obtenue par séchage de la suspension aqueuse selon l'une quelconque des revendications 16 à 20, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET supérieure à 15 m²/g.
22. Substance minérale contenant du carbonate de calcium modifié en surface selon la revendication 21, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET d'environ 20 m²/g à environ 200 m²/g, de préférence d'environ 30 m²/g à environ 150 m²/g, plus préférablement d'environ 40 m²/g à environ 100 m²/g.
23. Substance minérale contenant du carbonate de calcium modifié en surface selon la revendication 21, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a un diamètre de grain médian de 4 µm à environ 100 µm, de préférence d'environ 5 µm à environ 75 µm, plus préférablement d'environ 10 µm à environ 50 µm, encore plus préférablement d'environ 15 µm à environ 30 µm, déterminé par un appareil Mastersizer de Malvern.
24. Substance minérale contenant du carbonate de calcium modifié en surface selon la revendication 21, dans laquelle ladite substance minérale contenant du carbonate de calcium modifié en surface a une surface spécifique BET de 30 m²/g à environ 90 m²/g et un diamètre de grain médian de 10 µm à 50 µm, d déterminé par un appareil Mastersizer de Malvern.
25. Utilisation de la substance minérale contenant du carbonate de calcium modifié en surface de la suspension aqueuse selon l'une quelconque des revendications 16 à 20, ou de la substance minérale sèche en forme de billes contenant du carbonate de calcium modifié en surface selon l'une quelconque des revendications 21 à 24, dans le papier, le couchage du papier, le papier de soie, le papier photo numérique, les peintures, les revêtements, les adhésifs, les plastiques, le traitement des eaux usées ou les agents de traitement des eaux usées.
26. Utilisation selon la revendication 25, en tant qu'agent de matage dans les peintures et les revêtements.
27. Utilisation selon la revendication 26, dans laquelle l'agent de matage est présent en des quantités de 1 à 10 % en

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poids, de préférence de 2 à 7 % en poids, plus préférablement de 3 à 5 % en poids, sur la base de la peinture humide.

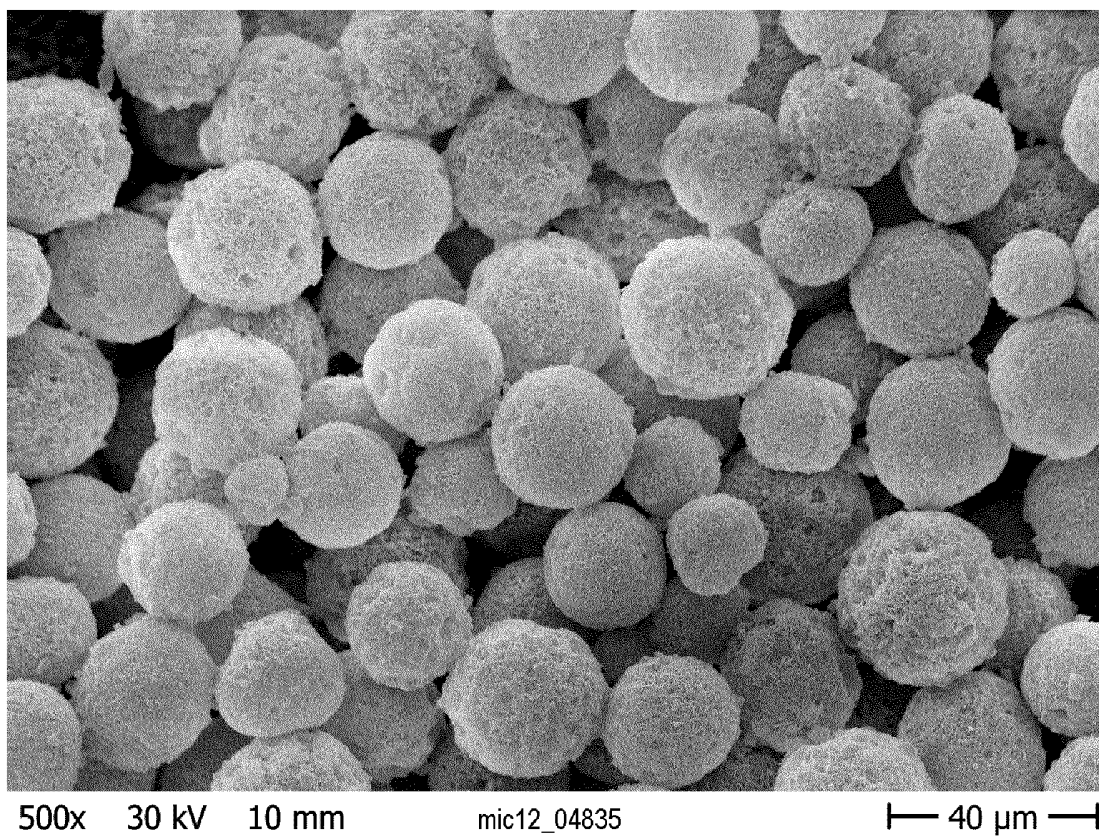
28. Utilisation selon la revendication 27, dans laquelle la surface de la peinture ou du revêtement étalé a une brillance à 85° comprise dans la plage inférieure à 10, de préférence de 0,5 à 9,5, plus préférablement de 1 à 8, encore plus préférablement de 2 à 6,5, lorsqu'elle est mesurée selon la norme DIN 67 530.

29. Papier, papier de soie, papier photo numérique, peintures, revêtements, adhésifs, plastiques ou adjuvant pour eaux usées comprenant la substance minérale en forme de billes contenant du carbonate de calcium modifié en surface de la suspension aqueuse selon l'une quelconque des revendications 16 à 20, ou la substance minérale sèche en forme de billes contenant du carbonate de calcium modifié en surface selon l'une quelconque des revendications 21 à 24.



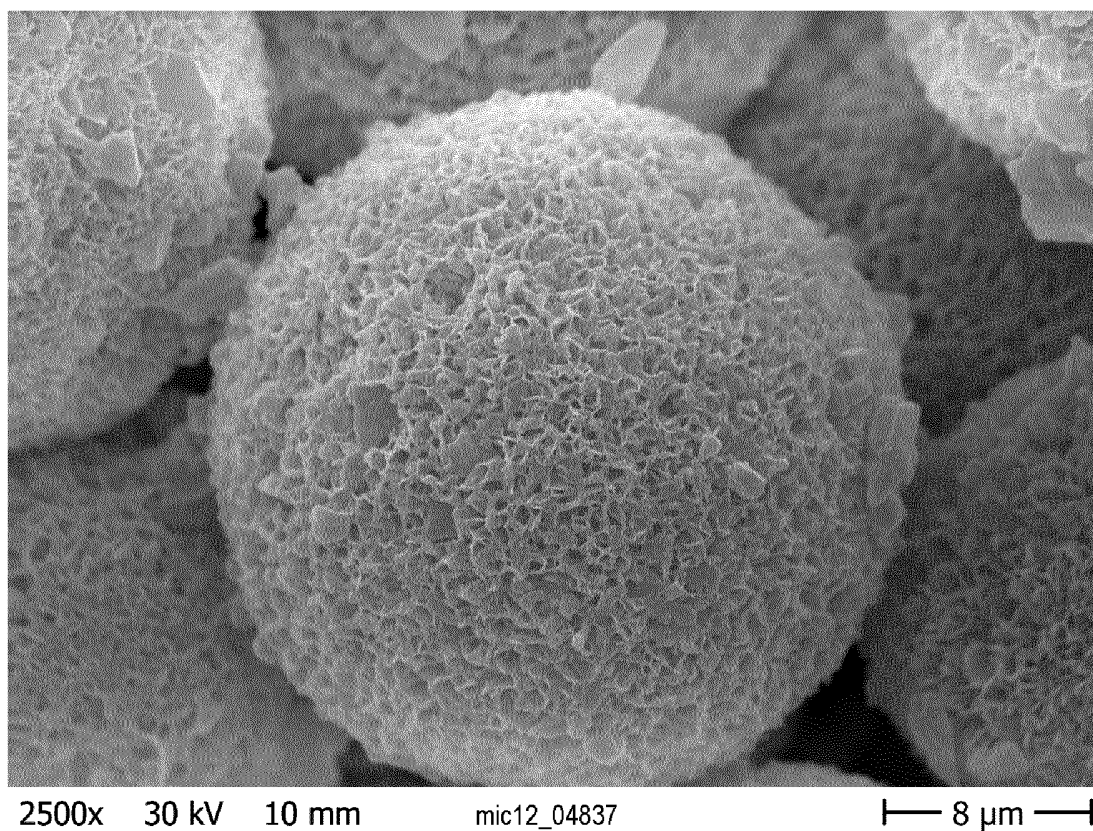
Particle Size Distribution Curve as per Malvern Mastersizer

Figure 1



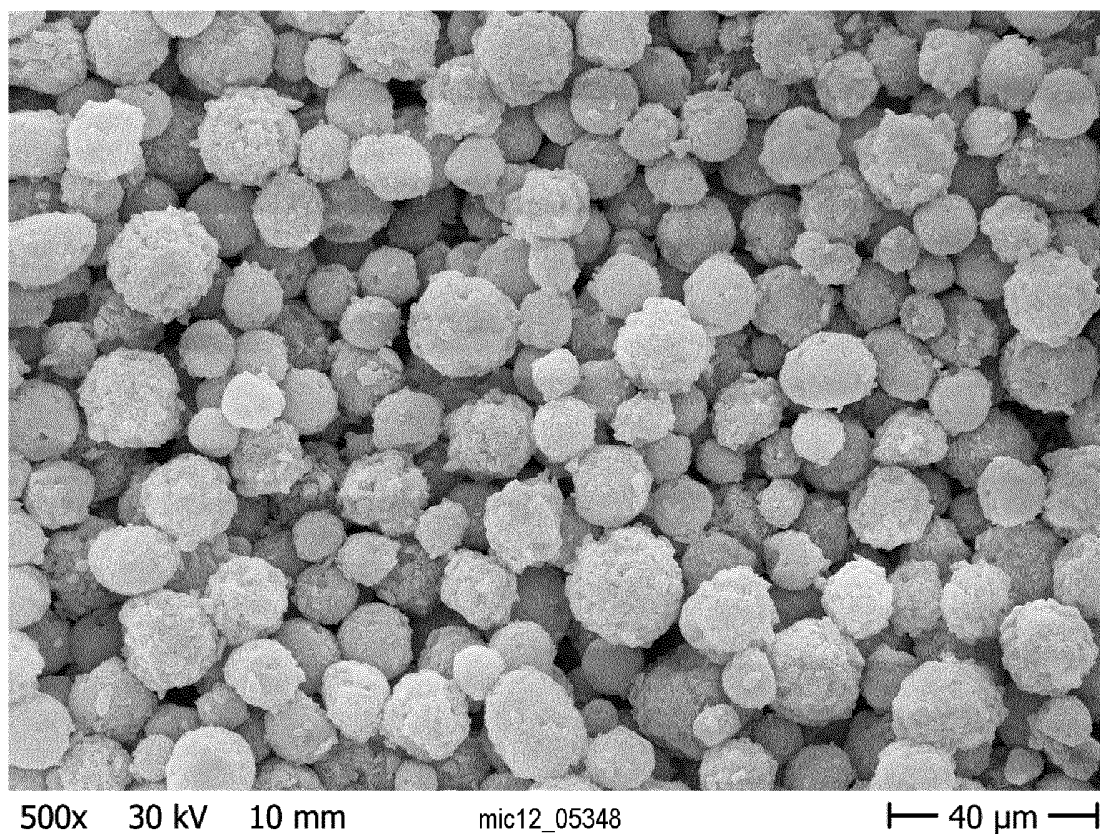
SEM x500 magnification of example E2. Ball-shaped surface modified CaCO_3 comprising minerals.

Figure 2a



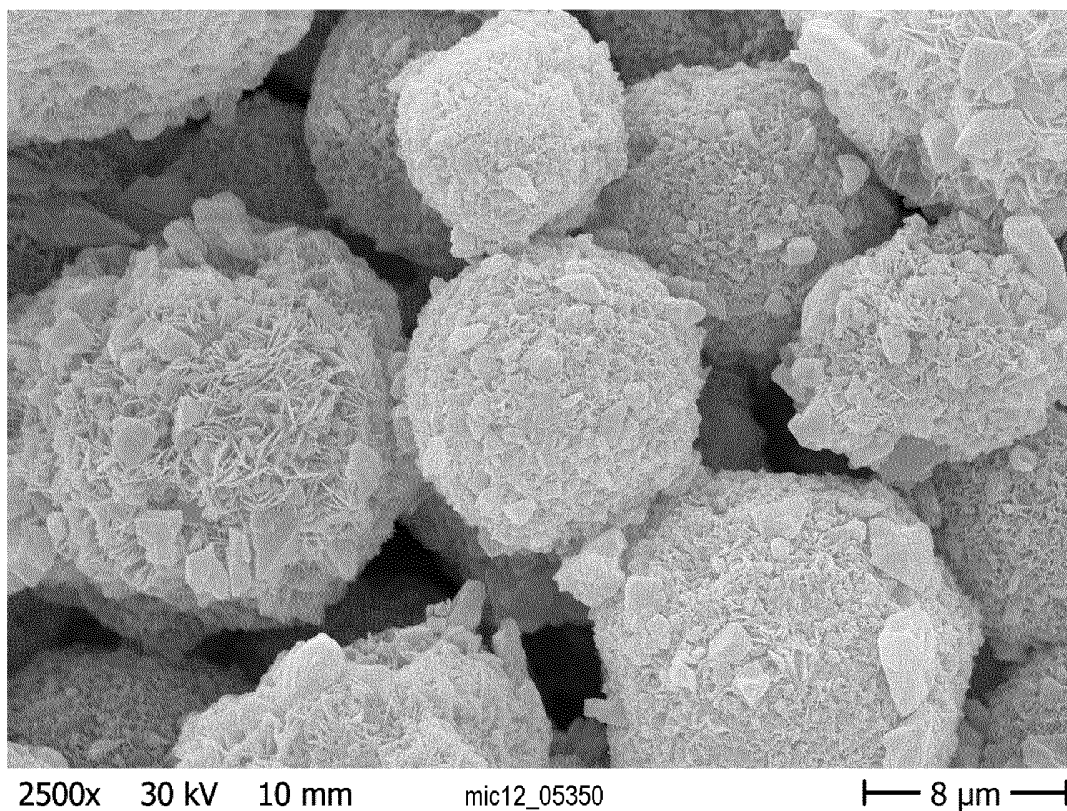
**SEM x2500 magnification of Example E2. Ball-shaped surface modified
CaCO₃ comprising minerals.**

Figure 2b



SEM x500 magnification of Example E6. Ball-shaped surface modified CaCO_3 comprising minerals.

Figure 3a



**SEM x2500 magnification of Example E6. Ball-shaped surface modified
CaCO₃ comprising minerals.**

Figure 3b

REFERENCES CITED IN THE DESCRIPTION

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Felületmódosított kalcium-karbonátot tartalmazó ásványok és azok alkalmazása

SZABADALMI IGÉNYPONTOK

1. Eljárás gömb-alakú gömbölyű felületmódosított kalcium-karbonát tartalmú részecskék előállítására, mely eljárás az alábbi lépéseket tartalmazza:

- a) legalább egy, vizes kalcium-karbonátot tartalmazó vizes ásványi iszapot biztosítunk;
- b) legalább egy vízzoldható savat biztosítunk;
- c) adott esetben külső forrásból további CO_2 gázt biztosítunk;
- d) az a) lépés szerinti, említett, kalcium-karbonátot tartalmazó vizes ásványi iszapot a b) lépés szerinti említett savval és in situ képződött és/vagy a c) lépés szerint kívülről betáplált CO_2 -vel keverés közben érintkeztetjük;
- e) adott esetben a vizes iszapot vízmentesítjük;

ahol legalább egy feldolgozási anyagot az a) lépés szerinti vizes kalcium-karbonát tartalmú ásványi iszapnak a b) lépés szerinti savval és a c) lépés szerinti in situ képződött, vagy kívülről betáplált CO_2 -vel való érintkeztetése előtt, alatt vagy után adagolunk, és

ahol a legalább egy feldolgozási anyagot a vas(II)szulfát, vas(III)szulfát, vas(II)klorid, vas(III)klorid, alumíniumsulfát és/vagy hidratált formáik csoportból választunk ki, és

ahol a feldolgozási anyag hozzáadott mennyisége legfeljebb 8 tömeg%, az iszap száraz tömegére vonatkoztatva.

2. Az 1. igénypont szerinti eljárás, ahol az említett, kalcium-karbonátot tartalmazó ásványt a márvány, kréta, mészkő, dolomit, kicsapott kalcium-karbonát (PCC) és ezek keverékei csoportból választjuk ki.

3. Az 1. vagy 2. igénypont szerinti eljárás, ahol az említett, kalcium-karbonát tartalmú ásvány az iszapban $0,01\mu\text{m}$ - $10\mu\text{m}$, előnyösen $0,2\mu\text{m}$ - $2\mu\text{m}$, még előnyösebben $0,5\mu\text{m}$ - $1\mu\text{m}$ tömegre alapozott átlagos szemcse átmérővel rendelkezik.

4. Az 1-3. igénypontok bármelyike szerinti eljárás, ahol az a) lépés szerinti említett iszap szilárd anyag tartalma nagyobb, mint 4 tömeg%, előnyösen 5 tömeg% és körülbelül 20 tömeg% közötti, az iszap tömegére vonatkoztatva.

5. Az 1-4. igénypontok bármelyike szerinti eljárás, ahol az említett, a) lépés szerinti iszap egy vagy több diszpergálószer hozzáadásával stabilizáljuk.

6. Az 1-5. igénypontok bármelyike szerinti eljárás, ahol a legalább egy, b) lépés szerinti vízzoldható sav pK_s értéke 0-6, előnyösen 0-2,5.

7. Az 1-6. igénypontok bármelyike szerinti eljárás, ahol a b) lépés szerinti, legalább egy vízzoldható savat a foszforsav, citromsav, bórsav, vagy ezek elegyei közül választjuk ki.

8. Az 1-7. igénypontok bármelyike szerinti eljárás, ahol a legalább egy vízzoldható savat a kalcium-karbonát tartalmú ásványi molekulaszámára vonatkoztatva 0,1 mol/mol – körülbelül 1 mol/mol, előnyösen 0,1-0,6 mol/mol moláris mennyiségben adagoljuk.

9. Az 1-8. igénypontok bármelyike szerinti eljárás, ahol a b) lépésben biztosított legalább egy vízzoldható savat egy vagy több lépésben, előnyösen egy lépésben adjuk az említett vízes, kalcium-karbonátot tartalmazó ásványi iszaphoz.

10. Az 1-9. igénypontok szerinti eljárás, ahol a b) lépés szerinti, legalább egy vízzoldható sav adagolását és az a) lépés szerinti vízes, kalcium-karbonátot tartalmazó ásványi iszap érintkeztetését a b) lépés szerinti savval és a c) lépés szerinti in situ képződött és/vagy kívülről betáplált CO_2 -vel keverő reaktorban végezzük, keverési körülmények között, úgy, hogy lényegében lamináris áramlás jön létre.

11. Az 1-10. igénypontok bármelyike szerinti eljárás, ahol az eljárást vízes körülmények között folytatjuk le, 20°C feletti és azt tartalmazó, így például körülbelül 25°C – körülbelül 95°C hőmérsékleten, előnyösen körülbelül 30°C – körülbelül 80°C, még előnyösebben körülbelül 50°C – körülbelül 75°C hőmérséklet tartományban.

12. Az 1-11. igénypontok bármelyike szerinti eljárás, ahol a feldolgozási anyagot az iszap száraz tömegére vonatkoztatva 0,01 tömeg% - körülbelül 5 tömeg%, előnyösebben körülbelül 0,05 tömeg% - körülbelül 4 tömeg%, még előnyösebben körülbelül 0,4 tömeg% - körülbelül 3 tömeg% mennyiségben adagoljuk.

13. Az 1-12. igénypontok bármelyike szerinti eljárás, ahol a feldolgozási anyagot, előnyösen alumínium-szulfátot vagy annak hidrátját, még előnyösebben alumínium-szulfát-hexadekahidrátot egy vagy több lépésben adagoljuk az említett vízes kalcium-karbonátot tartalmazó ásványi iszaphoz.

14. A 13. igénypont szerinti eljárás, ahol az alumínium-szulfát tartalom legfeljebb 5 tömeg%, az iszap száraz tömegére vonatkoztatva.

15. Az 1-14. igénypontok bármelyike szerinti eljárás, ahol a feldolgozási anyagot a b) lépés előtt, alatt vagy után adagoljuk.

16. Az 1-15. igénypontok bármelyike szerint előállított gömb-alakú felületmódosított kalcium-karbonát tartalmú ásvány vizes iszapja, ahol az említett felületmódosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete több mint $15\text{ m}^2/\text{g}$.

17. A 16. igénypont szerinti vizes iszap, ahol az említett felületmódosított kalcium-karbonát tartalmú ásvány átlagos szemcseátmérője $4\text{ }\mu\text{m}$ – körülbelül $100\text{ }\mu\text{m}$, előnyösen körülbelül $5\text{ }\mu\text{m}$ – körülbelül $75\text{ }\mu\text{m}$, még előnyösebben körülbelül $10\text{ }\mu\text{m}$ – körülbelül $50\text{ }\mu\text{m}$, és ennél is előnyösebben körülbelül $15\text{ }\mu\text{m}$ – körülbelül $30\text{ }\mu\text{m}$, Malvern Mastersizer szemcseméret analízátorral meghatározva.

18. A 16. vagy 17. igénypont szerinti vizes iszap, ahol az említett módosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete körülbelül $20\text{ m}^2/\text{g}$ – körülbelül $200\text{ m}^2/\text{g}$, előnyösen körülbelül $30\text{ m}^2/\text{g}$ – körülbelül $150\text{ m}^2/\text{g}$, még előnyösebben körülbelül $40\text{ m}^2/\text{g}$ – körülbelül $100\text{ m}^2/\text{g}$.

19. A 18. igénypont szerinti vizes iszap, ahol az említett módosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete $30\text{ m}^2/\text{g}$ – körülbelül $90\text{ m}^2/\text{g}$, és átlagos szemcseátmérője $10\text{ }\mu\text{m}$ - $50\text{ }\mu\text{m}$, Malvern Mastersizer szemcseméret analízátorral meghatározva.

20. A 16-19. igénypontok bármelyike szerinti vizes iszap, ahol a gömb-alakú felületmódosított kalcium-karbonát tartalmú ásvány d_{98}/d_{50} szűk szemcseméret eloszlása előnyösen kisebb, mint 3, előnyösebben kisebb, mint 2,5, előnyösen 1,4-2,9 tartományban van.

21. A 16-20. igénypontok bármelyike szerinti vizes iszap szárításával kapott, felületmódosított kalcium-karbonát tartalmú ásvány, ahol az említett felületmódosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete nagyobb, mint $15\text{ m}^2/\text{g}$.

22. A 21. igénypont szerinti, felületmódosított kalcium-karbonátot tartalmazó ásvány, ahol a felületmódosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete körülbelül $20\text{ m}^2/\text{g}$ – körülbelül $200\text{ m}^2/\text{g}$, előnyösen körülbelül $30\text{ m}^2/\text{g}$ – körülbelül $150\text{ m}^2/\text{g}$, még előnyösebben körülbelül $40\text{ m}^2/\text{g}$ – körülbelül $100\text{ m}^2/\text{g}$.

23. A 21. igénypont szerinti, felületmódosított kalcium-karbonátot tartalmazó ásvány, ahol a felületmódosított kalcium-karbonát tartalmú ásvány átlagos szemcseátmérője $4\text{ }\mu\text{m}$ – körülbelül $100\text{ }\mu\text{m}$, előnyösen körülbelül $5\text{ }\mu\text{m}$ – körülbelül $75\text{ }\mu\text{m}$, még előnyösebben körülbelül $10\text{ }\mu\text{m}$ – körülbelül $50\text{ }\mu\text{m}$, még ennél is előnyösebben körülbelül $15\text{ }\mu\text{m}$ – körülbelül $30\text{ }\mu\text{m}$, Malvern Mastersizer szemcseméret analízátorral meghatározva.

24. A 21. igénypont szerinti, felületmódosított kalcium-karbonátot tartalmazó ásvány, ahol a felületmódosított kalcium-karbonát tartalmú ásvány BET fajlagos felülete $30\text{ m}^2/\text{g}$ –

körülbelül $90 \text{ m}^2/\text{g}$, és átlagos szemeseátmérője $10 \mu\text{m} - 50 \mu\text{m}$, Malvern Mastersizer szemcseméret analízátorral meghatározva.

25. A 16-20. igénypontok bármelyike szerinti vizes iszap felületmódosított kalcium-karbonátot tartalmazó ásványának vagy a 21-24. igénypontok bármelyike szerinti száraz, gömb-alakú kalcium-karbonát tartalmú ásványnak az alkalmazása, papír, papír-bevonat, selyempapír, digitális fotó-papír, festékek, bevonatok, ragasztók, műanyagok, hulladék víz kezelés vagy hulladék vízkezelő szer céljára.

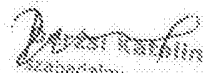
26. A 25. igénypont szerinti alkalmazás mattító szerként festékekben és bevonatokban.

27. A 26. igénypont szerinti alkalmazás, ahol a mattító szer 1-10 tömeg%, előnyösen 2-7 tömeg%, még előnyösebben 3-5 tömeg% mennyiségben van jelen, a nedves festék tömegére vonatkoztatva.

28. A 27. igénypont szerinti alkalmazás, ahol a száraz festék vagy bevonat fénye 85° -nál 10 alatti, előnyösen 0,5-9,5, előnyösebben 1-8, még előnyösebben 2-6,5, DIN 67 530 szabvány szerint mérve.

29. A 16-20. igénypontok bármelyike szerinti vizes iszap gömb-alakú felületmódosított kalcium-karbonátot tartalmazó ásványát vagy a 21-24. igénypontok bármelyike szerinti száraz, gömb-alakú kalcium-karbonát tartalmú ásványt tartalmazó papír, selyempapír, digitális foto-papír, festékek, bevonatok, ragasztóanyagok, műanyagok, vagy hulladék vízkezelő szerek.

A meghatalmazott


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