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(54) Titre : PROCEDE DE FABRICATION DE CARBONATE DE CALCIUM CO-BROYE
(54) Title: PROCESS OF MANUFACTURING CO-GROUND CALCIUM CARBONATE

(57) Abrégé/Abstract:
An object of the present invention is to provide a process to obtain a calcium carbonate material comprising GCC and PCC, with a specific steepness factor (defined as d_{30} / d_{70} x 100, where d_x is the equivalent spherical diameter relative to which x % by weight of the particles are finer) of at least about 30, preferably of at least about 40, and most preferably of at least about 45, in a cost efficient manner, wherein GCC and PCC are co-ground, possibly with at least another mineral material. Another object of the present invention lies in the obtained co-ground calcium carbonate material in the form of an aqueous suspension and in the form of a dry product. Another object of the present invention lies in the uses of such products in any sector making use of mineral materials, and notably in the paper, paint and plastic industries.

ABSTRACT

An object of the present invention is to provide a process to obtain a calcium carbonate material comprising GCC and PCC, with a specific steepness factor (defined as d_{30} / d_{70} x 100, where d_x is the equivalent spherical diameter relative to which x % by weight of the particles are finer) of at least about 30, preferably of at least about 40, and most preferably of at least about 45, in a cost efficient manner, wherein GCC and PCC are co-ground, possibly with at least another mineral material. Another object of the present invention lies in the obtained co-ground calcium carbonate material in the form of an aqueous suspension and in the form of a dry product. Another object of the present invention lies in the uses of such products in any sector making use of mineral materials, and notably in the paper, paint and plastic industries.

PROCESS OF MANUFACTURING CO-GROUND CALCIUM CARBONATE

It is an object of the present invention to provide a process to obtain a calcium carbonate material comprising GCC (ground calcium carbonate) and PCC (precipitated calcium carbonate). Such material is appropriate for use in a number of domains, for example in the paper industry.

It is also an object of the present invention to provide a process to obtain a calcium carbonate material comprising GCC and PCC, with a specific steepness factor (defined as d_{30} / d_{70} x 100, where d_x is the equivalent spherical diameter relative to which x % by weight of the particles are finer) of at least about 30, preferably of at least about 40, and most preferably of at least about 45. Such a material leads to superior properties of the paper coated with such a material, notably in terms of gloss.

It is also an object of the present invention to provide a process to obtain a calcium carbonate material comprising GCC and PCC, with a steepness factor of at least about 30, preferably of at least about 40, and most preferably of at least about 45, in a cost efficient manner, wherein GCC and PCC are co-ground, possibly with at least another mineral material.

Another object of the present invention lies in the co-ground calcium carbonate material (i.e. : aqueous mineral slurries containing the co-ground GCC and PCC and dry products containing the co-ground GCC and PCC) obtained through this process.

Another object of the present invention lies in the uses of such products in any sector making use of mineral materials, and notably in the paper, paint and plastic industries.

Many types of mineral are used in the paper coating formulations for the paper industry. Clay has traditionally been used for this purpose due to its low cost relative to other mineral pigments.

Calcium carbonate ($CaCO_3$) is used as both a coating and filling pigment, and is notably known to improve some of the optical properties of the final product, such as gloss, opacity or brightness. Calcium carbonate can be of two types: ground or natural calcium carbonate referred to as GCC, and synthetic or precipitated calcium carbonate referred to as PCC.

Ground calcium carbonate is calcium carbonate obtained from natural sources, such as limestone, marble or chalk, and processed through a treatment such as grinding. Precipitated calcium carbonate is a synthesized material, generally obtained by precipitation following reaction of carbon dioxide and lime in an aqueous environment. This PCC may be rhombohedral and/or scalenohedral and/or aragonitic. According to the needs of the man skilled in the art, this GCC or PCC may additionally be surface treated, for example with stearine

For many years, there has been need to supply the skilled man in the art with mineral slurries comprising GCC and PCC, since it may be of interest that both be present in the paper coating formulations, in order to regulate more precisely the final properties of the coated paper. Publications referring to the use of both natural and precipitated calcium carbonate in the paper industry include, for instance, "PCC or GCC, factors determining calcium carbonate choice in alkaline conversion" (published following the November 1995 28th Pulp and Paper Annual Meeting) and "GCC vs. PCC as the primary filler for uncoated and coated wood-free paper" (Tappi Journal 2000, 83(5), pp 76) : these publications refer to the properties of PCC/GCC blends for use in paper industry. In "Chalk : a calcium carbonate for the high-filled sheet" (TAPPI Proceedings, April 5-8 1992, Papermakers Conference, Book 2, Opryland Hotel, Nashville TN, , TAPPI Press, pp. 515-520), the author suggests that drawbacks associated with PCC may be overcome by using this mineral in conjunction with other fillers, such as GCC. Finally, in "Coating structure with calcium carbonate pigments and its influence on paper and print gloss" (Pulp & Paper Canada, 2004, 105(9), pp. 43-46), the influence of different pigment blends including GCC and PCC on paper properties including gloss and print gloss is investigated. The Applicant underlines that these publications appear to belong to the technical background of the invention, since they attest to the need to obtain mixtures of GCC and PCC for use in paper industry.

However, none of these publications teach or reveal the co-grinding of both GCC and PCC, and the further possibility to obtain a co-ground product with a specific steepness factor, which is one of the objects of the present invention.

With further reference to the need of the skilled man in the art to improve some of the final properties of the coated paper, there is also an additional need for the skilled man to improve some of the optical properties of the final product, such as gloss. Faced with this requirement, the skilled man in the art knows that the "steepness factor" of the mineral material used in the paper coating formulation is a criteria of main importance: the selection of specific values for the steepness factor, in relation with the choice of a specific mineral material, can lead to an improvement in the optical properties of the coated paper. At this point, the Applicant indicates that a common way to define the steepness factor is "the ratio of the d_x equivalent spherical diameter (at which x % by weight of the particles are finer) to the d_y equivalent spherical diameter (at which y % by weight of the particles are finer), multiplied by 100. In such a way, for a given mineral material in slurry form or in the form of a dry powder, the steepness factor can be regarded the steepness of the corresponding granulometric curve.

In this area, the skilled man in the art knows WO 2003 / 089 524, which targets a high degree of brightness, whiteness, and fluorescence in paper coatings or filler compositions used in cellulose based substrate and light weight coating base paper. The proposed solution consists of a hydrous kaolin having a GE brightness of at least 90 and a steepness factor (d_{30}/d_{70} x 100) of at least about 39. It has to be noted that this document does not offer teachings relating to calcium carbonate, since one of the requirements of the inventors is precisely to avoid the use of this mineral.

The prior art also reveals some documents dealing with the use of calcium carbonate of a single-type, in conjunction with specific steepness factors. EP 0 894 836 discloses a slurry consisting of water, commercially available dispersant which prevents the dissociation of agglomerated pigment in the slurry, and agglomerated carbonate-containing pigment with a particle size distribution in which 80-99 % by weight are below 2 μm in size, 50-90 % by weight are below 1 μm and 0-10 % by weight are below 0.2 μm, a steepness factor (ratio of diameter at 50 % by weight to diameter at 20 % by weight) is of 1.5-2.0 and a porosity is of 45-65 %. It is clearly that this invention

deals solely with natural calcium carbonate of the calcite, marble and chalk-type; moreover, the invention lies in a dispersing process and does not teach the grinding of the abovesaid carbonate-containing pigment. US 2002 155 055 addresses the problem of reducing the width of particle size distribution of calcium carbonate compositions for use in paper, but is exclusively focused on ground calcium carbonate, as recognized by the inventors (see [0007]). The proposed solution lies in a process comprising the step of forming a dispersant-free aqueous suspension of natural calcium carbonate, wet-grinding the suspension to produce a calcium carbonate composition having steepness ratio (A) and aging the suspension at temperature below 35 ° C to produce a calcium carbonate composition having steepness ratio (B) smaller than the ratio (A). In this document, the steepness factor is defined as the average diameter of the particles in the 75 % mass divided by the average diameter of the particles in the 25 % mass, when the size distribution is represented using a Sedigraph™.

There are also prior art documents which deal with the use of calcium carbonate of a single type or of both types (GCC and PCC blends), in conjunction with at least one other mineral matter (and notably kaolin), and disclosing some particular values for the steepness factor of each material and / or of the final blend. WO 2003 / 093 577 teaches that, in order to improve gloss, opacity, brightness and smoothness of paper, specific particulate pigments may be useful in the paper coating formulations. These pigments comprise a first component, which is PCC and a second component which is a processed particulate hydrous kaolin clay having a shape factor of at least 25 and a steepness of at least 20, or a first component, which is a PCC having a spherical particle shape and a second component which is a processed particulate hydrous kaolin clay having a shape factor at least 45, and a mean equivalent particle diameter of less than 0.5 μm, or a first component which is a PCC and a second component, which is a processed particulate hydrous kaolin clay having a shape factor less than 25. Moreover, WO 2002 / 016 509 teaches that to improve the optical properties of paper and printability of paper coatings, it is advantageous to use kaolin having a mean particle size of 0.7-3 μm and a shape factor of at least 60 ; this type of kaolin can be used in combination with another filler such as talc, calcium sulfate and / or alkaline earth metal carbonate. Finally, WO 2000 / 066 510 teaches that pigment compositions comprising a blend of a fine kaolin produced from block kaolin clay, and a calcium

carbonate which may be either GCC or PCC, wherein both particles have a median particle size less than 0.8 μm, and a steepness factor, defined as 100 x d_{30}/d_{70}, greater than 38, and wherein the kaolin / carbonate weight ratio is of 40/60, preferably of 50/50, can improve the optical properties and printability of coated paper. While the latter three documents refer to the use of blends of calcium carbonate (possibly of both the GCC and PCC type), and necessarily kaolin, which is not a requirement of the present invention, they do not teach nor reveal the possibility to co-grind PCC and GCC, or even to the possibility of co-grinding kaolin with at least one type of calcium carbonate mineral.

Closer from the scope of the present invention, there are also documents dealing with the use of mixtures of GCC and PCC, notably for use in paper formulations to enhance some of the optical properties of the coated paper. DE 4 128 570 discloses a carbonate filler and pigment with specified particle shape and size for filling and coating paper, giving high opacity, degree of whiteness and filler content. Such carbonate filler and pigment have a rhombohedral or round particle shape, a gradient factor (ratio of particle diameter in μm at 50 / 20 weight %) of 1.1-1.4, a ratio R of % particles finer than 1 μm / % particles finer than 0.6 μm ranging from 8 to 19, and average statistic particle diameter ranging from 0.4 to 1.5 μm. Finally, WO 2004 / 059 079 discloses particulate pigment compositions, useful in paper, comprising a first pigment which is ground calcium carbonate and a second pigment which is precipitated or ground calcium carbonate, carbonate, the first and second pigments having different size distribution steepness factors (100 x d_{30}/d_{70}). More precisely, the claimed particulate pigment composition comprises two pigment components. The first comprises particulate GCC carbonate having a steepness factor of 30-45, and the second comprises PCC with a steepness factor of 55-75, and diameter of at most 0.5 μm, or GCC with a steepness factor of 40-55.

First, it must be noted that neither of these two documents reveals a specific steepness factor of the final product, which is one of the objects of the present invention. Secondly, none of these documents teaches the co-grinding of GCC and PCC. It appears clearly that these inventions are based on the mixing of both GCC and PCC calcium carbonate types: the skilled man encounters new problems. Finely ground PCC with a certain granulometry is commonly desired, said granulometry being

achieved by grinding in dry and / or aqueous media. Nevertheless, after this grinding step, it has been observed that the resulting fine PCC particles collapse and must subsequently be de-agglomerated (processes in order to de-agglomerate such finely ground PCC are notably disclosed in JP 2001 089 505, JP 56 104 713, US 6 143 065 or US 5 279 663) by mechanical means and / or by the addition of de-agglomerating agents: this addition step represents an additional expense in the PCC production process ; there is a need to perform this de-agglomeration step in a cost-efficient manner. Finally, when co-grinding GCC and PCC as opposed to separately grinding each component prior to blending, in particular when using the specific ceria-containing beads described hereafter, a surprising increase in grinding efficiency (decrease in total specific energy required to obtain the final products with the desired steepness factor) has been observed.

As indicated above, there is a need to provide the skilled man in the art with mineral slurries comprising both GCC and PCC for use in paper manufacturing, the steepness factor of the corresponding mineral being selected so that optical properties of the coated paper are improved, and in a cost efficient way in order to avoid, notably, the additional costly step of de-agglomerating PCC as necessary in the case of simply mixing of GCC and PCC.

Via the present invention, a new process of manufacturing a calcium carbonate mineral material comprising both GCC and PCC, without the drawbacks present in the prior art, has surprisingly been found. This process lies in a process for the preparation of co-ground calcium carbonate material of the GCC and PCC type, presenting a steepness factor of at least about 30 %, preferably of at least about 40 %, and most preferably of at least about 45 %, comprising the step of co-grinding GCC and PCC, possibly with at least another mineral material.

In some implementations, there is provided a process of manufacturing co-ground calcium carbonate material comprising ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), the process comprising the steps of:

(a) providing GCC in an aqueous suspension;

(b) co-grinding the aqueous suspension of GCC and an aqueous suspension of PCC to obtain a co-ground calcium carbonate material having a steepness factor of at least 30, wherein the co-grinding of GCC and PCC is conducted in the presence of talc;

(c) optionally screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b); and

(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c).

In some implementations, there is provided a process of manufacturing co-ground calcium carbonate material comprising ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), the process comprising the steps of:

(a) providing GCC in an aqueous suspension;

(b) co-grinding the aqueous suspension of GCC and an aqueous suspension of PCC to obtain a co-ground calcium carbonate material having a steepness factor of at least 30, wherein the co-grinding of GCC and PCC occurs at a pH of above 11;

(c) optionally screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b); and

(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c).

The invention also provides a process of manufacturing a co-ground calcium carbonate material of the GCC and PCC type, presenting a steepness factor of at least about 30, preferably of at least about 40, and most preferably of at least 45, and characterised in that it comprises the steps of:

(a) providing at least one calcium carbonate material, optionally in the form of an aqueous suspension,

(b) co-grinding GCC and PCC, optionally with at least another mineral material,

(c) optionally screening and / or upconcentrating the co-ground calcium carbonate material obtained following step (b),

(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c)

This process allows the skilled man in the art to obtain co-ground calcium carbonate material in the form of an aqueous suspension and / or in the form of a dry product comprising both GCC and PCC, which may notably be used in the paper industry. Moreover, and due to the specific selection concerning the steepness factor of the final product, which must be of at least about 30, preferably of at least about 40, and most preferably of at least about 45, high gloss properties are achieved in the coated paper.

Lastly, it has surprisingly been found that following the co-grinding step, significant additional PCC de-agglomeration is no longer necessary : as such, the process according to the invention is less expensive than processes of the prior art based on the simple mixing of both GCC and PCC, which requires a first de-agglomeration of PCC.

Finally, when co-grinding GCC and PCC as opposed to separately grinding each component prior to blending, in particular when using the specific ceria-containing beads described hereafter, a surprising increase in grinding efficiency (decrease in total specific energy required to obtain the final products with the desired steepness factor) has been observed.

The Applicant would like also to mention EP 0 850 880, which discloses an aqueous slurry or dehydrated wet cake with a 25-75 % solids concentration comprising a mixture of PCC and a viscosity reducing agent which is dispersed in a mixer to give a slurry with a viscosity below 1000 cp (at 25 °C), and which comprises 0.2-3 μm median diameter calcium carbonate particles. The slurry is then admixed with 1.5-30 μm median diameter dry ground calcium carbonate particles to give a weight ratio of to(II) of 20 : 80 to 80 : 20 and a solids concentration of 60-85 %. The slurry is next dispersed in a mixer to a viscosity below 1000 cp and finally dispersed in a sand grinding mill to give a product aqueous slurry comprising 0.2-2 μm median diameter

calcium carbonate particles. The EP 0 850 880 patentee teaches the above process as a solution to counter the high shear rheology difficulties encountered when the GCC component is wet ground, which is a technical problem different than the one solved by the present invention. By contrast, in the present invention, it has firstly been found that a wet grinding is also acceptable without a loss of gloss. Furthermore, the patentee makes no reference to any gain in production process energy via this process that necessitates a dry grinding of GCC. Finally, this patent does not teach that a desirable steepness factor can be reached for gloss improvement by an energetically economic process.

A first object of the invention consists in a process of manufacturing a co-ground calcium carbonate material comprising GCC and PCC, presenting a steepness factor of at least about 30, preferably of at least about 40, and most preferably of at least about 45, and characterised in that it comprises the steps of :

(a) providing at least one calcium carbonate material, optionally in the form of an aqueous suspension,
(b) co-grinding GCC and PCC, optionally with at least another mineral material,
(c) optionally screening and / or upconcentrating the co-ground calcium carbonate material obtained following step (b),
(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c)

The process according to the invention is characterised in that in step (a), the calcium carbonate material is provided as an aqueous suspension, and in that this aqueous suspension contains from 20 % to 80 % by dry weight of calcium carbonate, preferably from 50 % to 75 %, and most preferably from 50 % to 70 %. Said aqueous suspension may result from the dispersion of calcium carbonate material in the form of a wet cake

According to this specific embodiment, the process according to the invention is also characterised in that the calcium carbonate material provided in the form of an aqueous suspension is GCC.

In this particular embodiment, the wet ground natural calcium carbonate may be subjected to a wet benefication step prior to step (b), allowing the removal of impurities, such as silicate impurities, for instance by froth flotation.

In another embodiment, the process according to the invention is also characterised in that step (c) is carried out.

In another embodiment, the process according to the invention is also characterised in that step (d) is carried out.

More generally, the process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 20 % to 80 % (by dry weight of calcium carbonate), preferably from 50 % to 75 %, and most preferably from 50 % to 70 %.

The process according to the invention is also characterised in that at least one dispersing and / or grinding aid agent present in a weight % relative to the total dry mineral material ranging from 0 to 2 %, preferably from 0.2 % to 1.4 %, and most preferably from 0.5 % to 1.2 % may be added before, during or after co-grinding in step b).

The skilled man in the art will choose the dispersing and / or grinding aid agent as a function of the properties he wishes to achieve. He can use, for instance, homopolymers of (meth)acrylic acid and / or copolymers of (meth)acrylic acid in combination with other water soluble monomers, such homo- and copolymers, which are totally or partially neutralised.

Such dispersants may be added to obtain a stable Brookfield™ viscosity of less than 3000 mPa.s, preferably of less than 1000 mPa.s measured at 25°C.

The process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b) is conducted in the presence of at least another mineral material selected from among talc, clay, Al_2O_3, TiO_2 or mixtures thereof.

More preferably, the other mineral material is selected among from talc, clay or mixtures thereof.

Most preferably, the other mineral material is talc or clay.

The process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b) occurs at a pH of above 7.

In another embodiment, the process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b) occurs at a pH of above 10.

In another embodiment, the process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b) occurs at a pH of above 11.

This pH increase can be the result of, for example, one or more of the following: by the addition of a base, preferably of a base of a mono or divalent cation, most preferably of sodium or calcium, by the addition of an alkaline preparation of a biocide, or by the release of hydroxide, such a $Ca(OH)_2$, during grinding of a material, such as during the co-grinding of PCC and GCC. The Applicant indicates that he knows of French patent application published as FR 2881064, which mentions biocides that may be added during the grinding step (b).

The process according to the invention is also characterised in that the grinder contents are subject to a temperature rise, to above 60°C, preferably to above 90°C, and most preferably to above 100°C, during step (b).

This temperature refers to the temperature reached by the mill contents at any one point in the mill. In particular, the mill contents at the mill base may be subject to a higher temperature as a result of a higher hydrostatic pressure.

The process according to the invention is also characterised in that the PCC present when co-grinding during step (b) accounts for 10% to 90% of the total combined

PCC and GCC weight, preferably from 20 % to 80 % of the total combined PCC and GCC weight, and most preferably from 30 % to 70 % of the total combined PCC and GCC weight.

The process according to the invention is also characterised in that the co-grinding of GCC and PCC during step (b), is conducted in the presence of ceria-containing zirconium oxide grinding beads as grinding media, such beads having :

- a ceria content of between 14 % and 20 % by weight relative to the total weight of said bead, preferably of between 15 % and 18 % by weight relative to the total weight of said bead, and most preferably of approximately 16 % by weight relative to the total weight of said bead; and

- an average grain size after sintering of the grains forming said beads of less than 1 μm, preferably of less than 0.5 μm, and most preferably of less than 0.3 μm.

This grain size is determined by analysis of scanning electron microscope images of the beads. Bead ceria content is analysed by ICP Optical Emission Spectrometry

The process according to the invention is also characterised in that the beads have an original diameter prior to grinding of between 0.2 mm and 1.5 mm, preferably of between 0.4 mm and 1.0 mm.

Another object of the present invention lies in the co-ground calcium carbonate material comprising GCC and PCC, characterised in that it is obtained by the process according to the invention.

Another object of the present invention lies in calcium carbonate material comprising GCC and PCC, characterised in that it is in the form of an aqueous suspension, and presents a steepness factor of at least about 30, preferably of at least about 40, and most preferably of at least about 45.

According to the above embodiment, the co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that it contains from 20 % to 80 % by dry weight of calcium carbonate material, preferably from 40 % to 75 % by dry weight of calcium carbonate material, and most preferably from 60 % to 70 % by dry weight of calcium carbonate material.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that the PCC present accounts for 10 % to 90 % of the total combined PCC and GCC weight, preferably from 20 % to 80 % of the total combined PCC and GCC weight, and most preferably from 30 % to 70 % of the total combined PCC and GCC weight.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that it features a d_{50} from about 0.2 μm to 2.0 μm, preferably from 0.2 μm to 0.8 μm, and most preferably from 0.25 μm to 0.45 μm. This d_{50} is measured using a Sedigraph™ 5100.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that the aqueous suspension contains at least one dispersing and / or grinding aid agent, such dispersing and / or grinding aid agent being present in a weight % relative to the total dry mineral material ranging from 0 to 2 %, preferably from 0.2 % to 1.4 %, most preferably from 0.5 % to 1.2 %.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that the slurry water passed through a 40 μm sieve contains less than 1000 ppm of ZrO_2 and less than 200 ppm CeO_2. ZrO2 and CeO2 contents are determined by ICP-OES.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that the slurry water features a ZrO_2/CeO_2 weight ratio of from 4 to 6.5, preferably of from 4.6 to 5.7, and most preferably of 5.3.

The co-ground calcium carbonate material in the form of an aqueous suspension is also characterised in that it contains :

- a fraction of particles finer than 1 μm of greater than 80 %, preferably of greater than 85 %, more preferably of greater than 90 %, and even more preferably of greater than 95 %, and
- a BET specific surface area of less than 25 m^2/g.

When the fraction of particles finer than 1 μm is greater than 95 %, the BET specific surface area is preferably less than 25 m^2/g. When the fraction of particles finer than 1 μm is greater than 90 %, greater than 85 %, and greater than 80 %, the BET specific surface area is preferably less than 20 m^2/g, less than 18 m^2/g, and less than 15 m^2/g, respectively.

Another object of the present invention lies in the co-ground calcium carbonate material comprising GCC and PCC, characterised in that it is in the form of a dry product, presenting a steepness factor of at least about 30, preferably of at least about 40, and most preferably of at least about 45.

The co-ground calcium carbonate material in the form of a dry product is also characterised in that the PCC present accounts for 10 % to 90 % of the total combined PCC and GCC weight, preferably from 20 % to 80 % of the total combined PCC and GCC weight, and most preferably from 30 % to 70 % of the total combined PCC and GCC weight.

The co-ground calcium carbonate material in the form of a dry product is also characterised in that it contains :

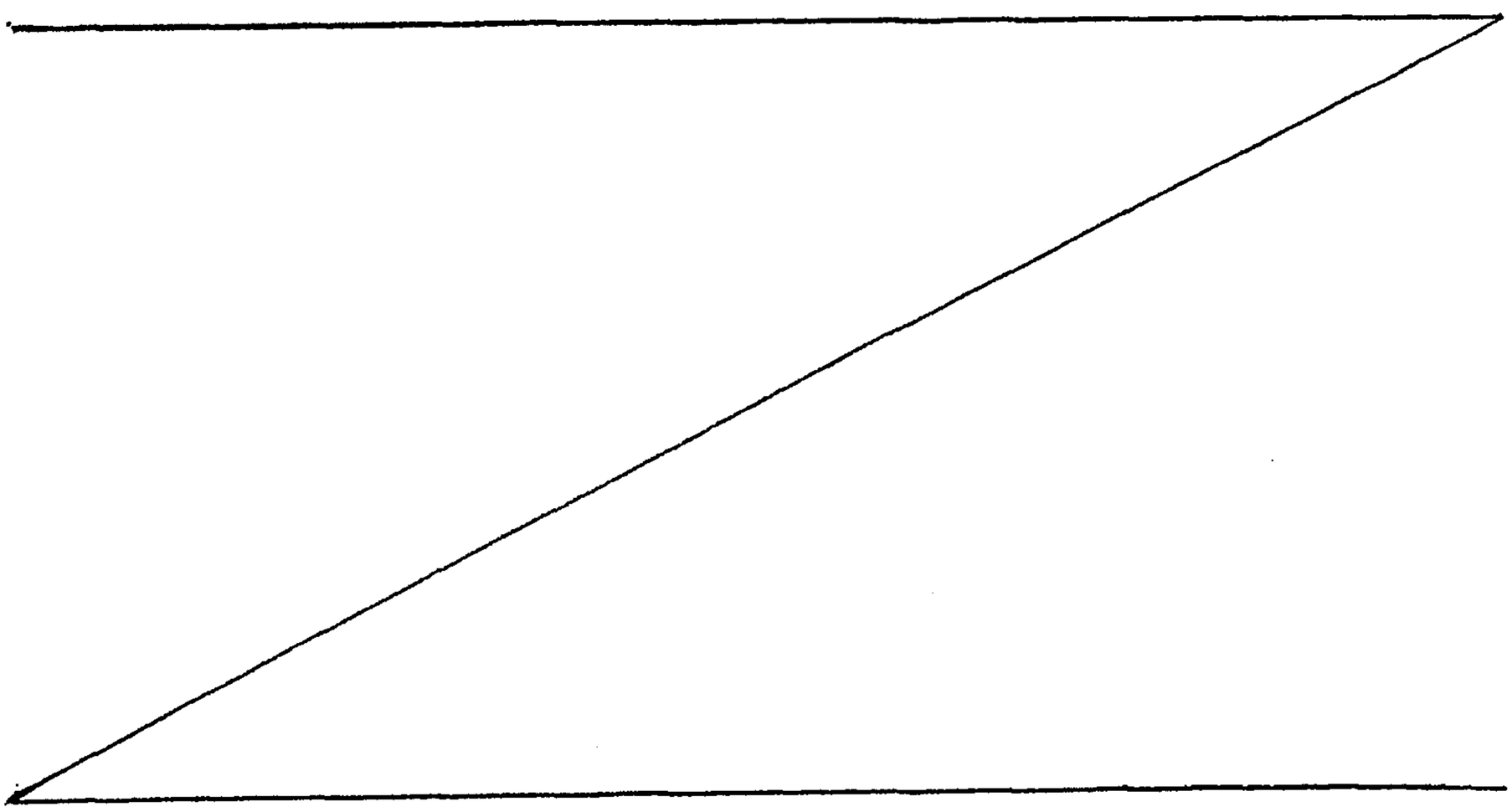
- a fraction of particles finer than 1 μm of greater than 80 %, preferably of greater than 85 %, more preferably of greater than 90 %, and even more preferably of greater than 95 %, and
- a BET specific surface area of less than 25 m^2/g.

When the fraction of particles finer than 1 μm is greater than 95 %, the BET specific surface area is preferably less than 25 m^2/g. When the fraction of particles finer than 1 μm is greater than 90 %, greater than 85 %, and greater than 80 %, the BET specific surface area is preferably less than 20 m^2/g, less than 18 m^2/g, and less than 15 m^2/g, respectively.

The co-ground calcium carbonate material in the form of a dry product is also characterised in that it features a d_{50} from about 0.2 μm to 2.0 μm, preferably from 0.2 μm to 0.8 μm, and most preferably from 0.25 μm to 0.45 μm. This d_{50} is measured using a Sedigraph™ 5100.

The co-ground calcium carbonate material in the form of a dry product is also characterised in that it features a ZrO_2/CeO_2 weight ratio of from 4 to 6.5, preferably of from 4.6 to 5.7, and most preferably of 5.3.

Finally, another object of the present invention lies in the use of the co-ground calcium carbonate material according to the invention, in any sector making use of mineral material, and notably in the paper, paint and plastic industries.



EXAMPLES

The following examples are intended to illustrate certain embodiments of the invention and are non-limitative.

Median diameter (d_{50}) and the fraction of particles featuring a diameter below a given diameter value were measured using a Sedigraph™ 5100.

Example 1 – Comparative Example

Ground calcium carbonate presenting a median diameter of 1.5 μm was wet-ground at a solids content of 74.5 % in the presence of the following additives: 1.51 % sodium polyacrylate, in a two-pass process using ceria-comprising zirconium oxide grinding beads featuring a median bead diameter of 0.45 mm, a CeO_2 content of 16 % by weight relative to the total bead weight, and a grain size after sintering of 0.4 μm (determined by evaluations of SEM images). The specific grinding energy required to obtain a final GCC with a steepness factor of about 35 % was of 270 kWh/t.

The obtained slurry of the ground GCC material featuring a subsequently diluted solids content of 75 % was then added to a standard paper coating formulation made up of the following proportions of components :

100 parts	ground GCC material
10.5 parts	SBR latex
0.5 parts	synthetic thickener
0.2 parts	polyvinyl alcohol
0.2 parts	optical brightening agent

The above coating was adjusted to a final solids content of 68 % and applied on a standard pre-coated wood-free base paper with a grammage of 71 g/m^2 at a coat weight of 10 g/m^2/side. This coated base paper was then calendered using a supercalender under the following calendering conditions: calender speed of 800 m/min, calender load of 200 kN/cm and a temperature of 105 °C.

The gloss of the coated paper surface was of 70 % Tappi 75°.

Example 2 – Illustration of the process according to the invention

A 76 % solids content slurry of ground calcium carbonate presenting a median GCC diameter of 1.4 μm was ground in the presence of a 51 % solids content PCC slurry with a median PCC diameter of 0.75 μm. The PCC to GCC weight ratio in the mill was of 50:50. The total solids content of the slurry in the mill was of 61 % and a median diameter of 1.1. The grinder contents were then co-ground in the presence of the following total additives content: 0.95 weight % sodium polyacrylate, using ceria-comprising zirconium oxide grinding beads featuring a median bead diameter of 0.45 mm, a CeO2 content of 16 % by weight relative to the total bead weight, and a grain size after sintering of 0.4 μm (determined by evaluations of SEM images). The specific grinding energy required to obtain a final co-ground product with a steepness factor of about % 42 was of 200 kWh/t.

The obtained slurry of the co-processed material featuring a solids content of 70.2 % was then added to a standard paper coating formulation made up of the following weight proportions of components :

100 parts	co-processed material
10.5 parts	SBR latex
0.5 parts	synthetic thickener
0.2 parts	polyvinyl alcohol
0.2 parts	optical brightening agent

The above coating was adjusted to a final solids content of 68 % and applied on a standard pre-coated wood-free base paper with a grammage of 71 g/m^2 at a coat weight of 10 g/m^2/side. This coated base paper was then calendered using a supercalender under the following calendering conditions: calender speed of 800 m/min, calender load of 200 kN/cm and a temperature of 105 °C.

The gloss of the coated paper surface was of 72 % Tappi 75°.

The above results are summarised in Table 1.

Table 1:

	Example 1	Example 2
Fraction of particles finer than 1 μm in the final ground product	97 %	97 %
BET specific surface area of the final ground product	28 g/m^2	23 g/m^2
Steepness factor of the final ground product	35	42
Median diameter of the final ground product	0.27 μm	0.27 μm
Total specific grinding energy required to produce the product	270 kWh/t	200 kWh/t
Tappi gloss of paper coated with a formulation comprising the product	70 %	72 %
Brightness of paper coated with a formulation comprising the product	95.1 %	96.5 %
Opacity of paper coated with a formulation comprising the product	89.7 %	90.2 %

Table 1 illustrates that the process according to the invention requires less specific grinding energy, and leads to an equal/improved gloss, relative to a process of the prior art.

Example 3 – Comparative example

This example illustrates a blend of PCC and GCC, in which each component is first separately ground prior to being mixed.

A 48 % solids aqueous slurry of PCC starting material having the characteristics indicated under Example 3 in Table 2 was ground in a media mill using yttrium-stabilised zirconium silicate grinding beads featuring a bead diameter prior to grinding of 0.6 to 1.0 mm. A total of 50 kWh/t specific grinding energy was expended in order to obtain a PCC end material having the end material characteristics indicated in Table

2. The final solids content of this subsequently upconcentrated PCC slurry was of 68 %.

Separately, a 74 % solids aqueous slurry of GCC starting material having the characteristics indicated under Example 3 in Table 2 was ground in a media mill using yttrium-stabilised zirconium silicate grinding beads featuring a bead diameter prior to grinding of 0.6 to 1.0 mm. A total of 210 kWh/t specific grinding energy was expended in order to obtain a GCC end material having the end material characteristics indicated in Table 2. The final solids content of this GCC slurry was of 75 %.

The PCC and GCC slurries were then mixed so as to obtain a PCC/GCC blend material with a PCC:GCC weight ratio of 30:70. This slurry was then added to a standard paper coating formulation made up of the following weight proportions of components :

100 parts	PCC/GCC blend material
10.5 parts	SBR latex
0.5 parts	synthetic thickener
0.2 parts	polyvinyl alcohol
0.2 parts	optical brightening agent

The above coating was adjusted to a final solids content of 68 % and applied on a standard pre-coated wood-free base paper with a grammage of 71 g/m^2 at a coat weight of 10 g/m^2/side. This coated base paper was then calendered using a supercalender under the following calendering conditions: calender speed of 800 m/min, calender load of 200 kN/cm and a temperature of 105°C.

The optical properties of the coated paper surface are given in Table 2.

Example 4 – Example according to the invention.

This example illustrates a co-ground PCC and GCC obtained by a process according to the invention.

A 74 % solids content slurry of ground calcium carbonate presenting the characteristics listed under Example 4 in Table 2 was ground in the presence of a 48 % solids content PCC slurry with the characteristics listed under Example 4 in Table 2 in a media mill. The PCC to GCC weight ratio in the mill was of 30:70 and the solids content of 65.9 %. The grinder contents were co-ground using yttrium-stabilised zirconium silicate grinding beads featuring a bead diameter prior to grinding of 0.6 to 1.0 mm. A total of 116 kWh/t specific grinding energy was expended in order to obtain a GCC/PCC co-ground end material having the end material characteristics indicated in Table 2. The final solids content of this GCC slurry was of 70.3 %.

This slurry was then added to a standard paper coating formulation made up of the following weight proportions of components :

100 parts	PCC/GCC co-ground material
10.5 parts	SBR latex
0.5 parts	synthetic thickener
0.2 parts	polyvinyl alcohol
0.2 parts	optical brightening agent

The above coating was adjusted to a final solids content of 68 % and applied on a standard pre-coated wood-free base paper with a grammage of 71 g/m^2 at a coat weight of 10 g/m^2/side. This coated base paper was then calendered using a supercalender under the following calendering conditions: calender speed of 800 m/min, calender load of 200 kN/cm and a temperature of 105°C.

The optical properties of the coated paper surface are given in Table 2.

Table 2:

Product Name		Example 3: PCC/GCC Blend Material	Example 4: PCC/GCC Co-Ground Material
Starting material characteristics			
GCC	d_{50} (µm)	1.4	1.4
	Steepness factor	28	28
PCC	d_{50} (µm)	0.75	0.75
	Steepness factor	55	55
End material characteristics			
GCC	d_{50} (µm)	0.40	--
	Steepness factor	34	--
PCC	d_{50} (µm)	0.38	--
	Steepness factor	40	--
PCC / GCC	PCC/GCC weight ratio	30/70	30/70
	d_{50} (µm)	0.38	0.40
	Steepness factor	37	38
	Fraction of particles with a diameter less than 2 µm (%)	89.5	88.8
	BET specific surface area (g/m^2)	18.1	18.2
Total specific grinding energy		162 kWh/t	116 kWh/t
Characteristics of paper coated with the end material			
Paper gloss (Tappi 75°)		70.5 %	72 %
Opacity		90.4 %	90.5 %
Brightness R457		97.9 %	97.9 %

Table 2 indicates that the process to prepare a co-ground PCC/GCC material according to the invention requires less grinding energy as compared to that required to prepare a comparable blend of PCC and GCC, without any loss or with an improvement in optical properties.

Example 5

This example illustrates the use of a process according to the invention wherein 3 minerals, a natural calcium carbonate a precipitated calcium carbonate and a clay, are co-ground with the use of ceria-containing zirconium oxide grinding beads with a ceria content of 16 % by weight relative to the total weight of said bead, an average grain size after sintering of the grains forming said bead of 0.4 µm, and a median bead diameter of 0,45 mm. The co-ground material is then added to a coating formulation used to coat a base paper, and the resulting gloss is measured.

The following materials were co-ground :

- a 74 % solids content slurry of ground calcium carbonate presenting a median GCC diameter of 1.4 µm and prepared using 0.27 % weight (by weight of dry GCC) of an homopolymer of acrylic acid,
- a 51 % solids content PCC slurry with a median PCC diameter of 0.8 µm and prepared using 0.7 % weight (by dry weight of PCC) of an homopolymer of acrylic acid,
- and a 68 % solids content slurry of clay commercialized by HUBER™ under the name Lithoprint™.
-

The weight ratio PCC:GCC:clay in the mill was of 45:45:10.

The total solids content of the slurry in the mill was of 72 % and the median diameter was of 0.4 and 0.5 µm for the 2 tests illustrating the invention.

The grinder contents were then co-ground in the presence of the following total additives content:

- respectively 0.4 and 0.2 weight % (by dry weight of mineral matter) of an homopolymer of acrylic acid, where 14 mol % of the carboxylic functions are neutralized by sodium hydroxyde, having a molecular weight of 5 600 g/mol, and a polydispersity equal to 2.4,
- using ceria-comprising zirconium oxide grinding beads featuring a median bead diameter of 0.45 mm, a CeO2 content of 16 % by weight relative to the total bead weight, and a grain size after sintering of 0.45 µm,

leading to a coground material exhibiting a median diameter respectively of 0.4 and 0.5 µm.

The 2 obtained slurry of the co-processed material was then added to a standard paper coating formulation made up of the following weight proportions of components :

100 parts	co-processed material
11 parts	SBR latex (DL 966 commercialized by DOW CHEMICALS™)
0.5 parts	synthetic thickener (CMC FF5 commercialized by FINNFIX™)

0.4 parts	polyvinyl alcohol (PVA 4-98 commercialized by CLARIANT™)
0.6 parts	optical brightening agent (Blancophor™ P commercialized by BAYER™)

The above coating was applied on a standard topcoat base paper with a grammage of 78 g/m^2 at a coat weight of 10 g/m^2/side. This coated base paper was then calendered using a supercalender under the following calendering conditions: calender speed of 300 m/min, calender load of 170 kN/m and a temperature of 80°C.

For the coground material exhibiting a median diameter of 0.4 μm, the gloss of the coated paper surface was of 73 % Tappi 75° and 45 % DIN 75°.
By comparison, the same coating manufactured with 100 parts of a GCC having a median diameter of 0.4 μm was of 70 % Tappi 75° and 35 % DIN 75°.

For the coground material exhibiting a median diameter of 0.5 μm, the gloss of the coated paper surface was of 68 % Tappi 75° and 40 % DIN 75°.
By comparison, the same coating manufactured with 100 parts of a GCC having a median diameter of 0.4 μm was of 63 % Tappi 75° and 33 % DIN 75°.

CLAIMS

1. A process of manufacturing co-ground calcium carbonate material comprising ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), the process comprising the steps of:

(a) providing GCC in an aqueous suspension;

(b) co-grinding the aqueous suspension of GCC and an aqueous suspension of PCC to obtain a co-ground calcium carbonate material having a steepness factor of at least 30, wherein the co-grinding of GCC and PCC is conducted in the presence of talc;

(c) optionally screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b); and

(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c).

2. The process of claim 1, wherein the co-ground calcium carbonate material presents a steepness factor of at least 40.

3. The process of claim 1 or 2, wherein the co-ground calcium carbonate material presents a steepness factor at least 45.

4. The process according to any one of claims 1 to 3, comprising a further step (c) of screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b).

5. The process according to claim 4, comprising a further step (d) of drying the co-ground calcium carbonate material obtained following step (c).

6. The process according to any one of claims 1 to 3, comprising a further step (d) of drying the co-ground calcium carbonate material obtained following step (b).

7. The process according to any one of claims 1 to 6, wherein in step (b) the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) are co-ground with at least one other mineral material.

8. The process according to claim 7, wherein the at least one other mineral material comprises clay, Al_2O_3, or TiO_2 or mixtures thereof.

9. The process according to claim 7, wherein the at least one other mineral material comprises clay.

10. The process according to claim 9, wherein the talc is the only mineral material present in the co-grinding of GCC and PCC.

11. The process according to claim 9, wherein the at least one other mineral material consists of the talc and clay.

12. The process according to any one of claims 1 to 11, wherein in step (a) the aqueous suspension contains from 20% to 80% by dry weight of calcium carbonate.

13. The process according to any one of claims 1 to 12, wherein in step (a), the aqueous suspension contains from 50% to 75% by dry weight of calcium carbonate.

14. The process according to any one of claims 1 to 13, wherein in step (a) the aqueous suspension contains from 50% to 70% by dry weight of calcium carbonate.

15. The process according to any one of claims 1 to 14, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 20 to 80% by dry weight of calcium carbonate.

16. The process according to any one of claims 1 to 15, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 50% to 75% by dry weight of calcium carbonate.

17. The process according to any one of claims 1 to 16, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during

step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 50% to 70% by dry weight of calcium carbonate.

18. The process according to any one of claims 1 to 17, wherein at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0% to 2%.

19. The process of claim 18, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0.2% to 1.4%.

20. The process of claim 18, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0.5% to 1.2%.

21. The process of any one of claims 18 to 20, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is added before, during or after co-grinding in step (b).

22. The process according to any one of claims 1 to 21, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) occurs at a pH of above 7.

23. The process according to claim 22, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) occurs at a pH of above 10.

24. The process according to claim 23, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) occurs at a pH of above 11.

25. The process according to any one of claims 1 to 24, wherein during the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) in step (b), grinder contents are subjected to temperature rises to above 90°C.

26. The process according to any one of claims 1 to 24, wherein during the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) in step (b), grinder contents are subjected to temperature rises to above 100°C.

27. The process according to any one of claims 1 to 26, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 10% to 90% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.

28. The process according to any one of claims 1 to 26, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 20% to 80% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.

29. The process according to any one of claims 1 to 26, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 30% to 70% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.

30. A process of manufacturing co-ground calcium carbonate material comprising ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), the process comprising the steps of:

(a) providing GCC in an aqueous suspension;

(b) co-grinding the aqueous suspension of GCC and an aqueous suspension of PCC to obtain a co-ground calcium carbonate material having a steepness factor of at least 30, wherein the co-grinding of GCC and PCC occurs at a pH of above 11;

(c) optionally screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b); and

(d) optionally drying the co-ground calcium carbonate material obtained following step (b) or (c).

31. The process of claim 30, wherein the co-ground calcium carbonate material presents a steepness factor of at least 40.

32. The process of claim 30 or 31, wherein the co-ground calcium carbonate material presents a steepness factor at least 45.

33. The process according to any one of claims 30 to 32, comprising a further step (c) of screening and/or upconcentrating the co-ground calcium carbonate material obtained following step (b).

34. The process according to claim 33, comprising a further step (d) of drying the co-ground calcium carbonate material obtained following step (c).

35. The process according to any one of claims 30 to 32, comprising a further step (d) of drying the co-ground calcium carbonate material obtained following step (b).

36. The process according to any one of claims 30 to 35, wherein in step (b) the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) are co-ground with at least one other mineral material.

37. The process according to claim 36, wherein the at least one other mineral material comprises clay, Al_2O_3, or TiO_2 or mixtures thereof.

38. The process according to claim 36, wherein the at least one other mineral material comprises clay.

39. The process according to claim 38, wherein the at least one other mineral material is clay.

40. The process according to any one of claims 30 to 39, wherein in step (a) the aqueous suspension contains from 20% to 80% by dry weight of calcium carbonate.

41. The process according to any one of claims 30 to 40, wherein in step (a), the aqueous suspension contains from 50% to 75% by dry weight of calcium carbonate.

42. The process according to any one of claims 30 to 41, wherein in step (a) the aqueous suspension contains from 50% to 70% by dry weight of calcium carbonate.

43. The process according to any one of claims 30 to 42, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step

(b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 20 to 80% by dry weight of calcium carbonate.

44. The process according to any one of claims 30 to 43, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 50% to 75% by dry weight of calcium carbonate.

45. The process according to any one of claims 30 to 44, wherein the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) during step (b) is conducted in aqueous medium, wherein the concentration of calcium carbonate ranges from 50% to 70% by dry weight of calcium carbonate.

46. The process according to any one of claims 30 to 45, wherein at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0% to 2%.

47. The process of claim 46, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0.2% to 1.4%.

48. The process of claim 46, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is present in a weight % relative to the total dry mineral material ranging from 0.5% to 1.2%.

49. The process of any one of claims 46 to 48, wherein the at least one dispersing aid agent, grinding aid agent or combination thereof, is added before, during or after co-grinding in step (b).

50. The process according to any one of claims 30 to 49, wherein during the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) in step (b), grinder contents are subjected to temperature rises to above 90°C.

51. The process according to any one of claims 30 to 50, wherein during the co-grinding of the ground calcium carbonate (GCC) and the precipitated calcium carbonate (PCC) in step (b), grinder contents are subjected to temperature rises to above 100°C.

52. The process according to any one of claims 30 to 51, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 10% to 90% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.

53. The process according to any one of claims 30 to 51, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 20% to 80% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.

54. The process according to any one of claims 30 to 51, wherein the precipitated calcium carbonate (PCC) present when co-grinding during step (b) accounts for 30% to 70% of the total combined ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) weight.