USE IN A PAINT OF A DRY-GROUND CALCIUM CARBONATE WITH A COPOLYMER OF (METH)ACRYLIC ACID WITH AN ALKOXY OR HYDROXY POLYALKYLENEGLYCOL GROUP

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Abstract:
The invention resides in the use in a paint of a calcium carbonate characterised in that it is obtained by dry-grinding, firstly, and in that it is dry-ground in the presence of a grinding aid agent which is a copolymer of (meth)acrylic acid with a monomer containing an alcoxy or hydroxy polyalkylene glycol group, secondly. The invention also concerns the paints thus obtained.
USE IN A PAINT OF A DRY-GROUND CALCIUM CARBONATE WITH A COPOLYMER OF (METH)ACRYLIC ACID WITH AN ALKYOXY OR HYDROXY POLYALKYLENEGLYCOL GROUP

[0001] The present invention concerns the field of paints, where the said paints contain at least one mineral matter which is a calcium carbonate obtained by dry grinding.

[0002] Grinding using a dry process (as opposed to in an aqueous medium) of calcium carbonate is described in the documents “Beitrag zur Aufklärung der Wirkungsweise von Malhilfsmitteln” (“Freiberger Forschungshefte” VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, Germany (1975)), and “Calcium Carbonate” (Birkhäuser Verlag, 2001).

[0003] This grinding, which leads to a reduction in the sizes of the individual particles of calcium carbonate by mechanical action, is assisted by grinding agents which can be classified into the following 3 categories.

[0004] The first comprises the weak acids (formic, acetic, lactic, adipic as mentioned in document FR 2 863 914, or stearic as indicated in document EP 0 510 890), and their salts (sodium lignin sulfonate, sodium acetate, etc.). The second includes the weak bases, and notably the amines (see document GB 2 179 268). The third, and the most commonly used, since it is the most effective, includes the glycol-based alcohols, including notably diethylene glycol illustrated in documents WO 2002/081 573 and US 2003/019 399.

[0005] Although they are still the most effective, the latter lead to calcium carbonates with a high quantity of volatile organic compounds (VOCs). For this reason, finding an alternative solution to these glycol-based grinding aid agents which is at least as effective as them in terms of the final application would constitute a major contribution to the state of the technique.

[0006] With this regard, a first object of the invention consists in the use, in a paint, of a calcium carbonate characterised in that the said carbonate is dry-ground in the presence of a grinding aid agent, firstly, and in that the grinding aid agent is, secondly, a copolymer, consisting:

[0007] a) of at least one anionic monomer chosen from among acrylic acid, methacrylic acid and their blends,

[0008] b) and of at least one non-ionic monomer, of formula (I):

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{R}_3 \quad \text{O}_{\mu} \quad \text{O}_{\nu} \quad \text{O}_{\pi} \quad \text{O}_{\omega} \quad \text{R'}
\end{align*}
\]

[0009] where:

[0010] m, n, p and q are integers such that: m, n, p\( \leq 150 \), q\( \leq 1 \), and 5\( \leq (m+n+p)q \leq 150 \), and preferably 15\( \leq (m+n+p)q \leq 120 \),

[0011] R\(_1\) represents hydrogen or the methyl or ethyl radical,

[0012] R\(_2\) represents hydrogen or the methyl or ethyl radical,

[0013] R represents a radical containing an unsaturated polymerisable function, preferentially belonging to the group of vinyls, or to the group of acrylic, methacrylic, maleic esters, or to the group of unsaturated urethanes such as acrylurethane, methacrylurethane, \( \alpha-\alpha' \)dimethyl-isopropenyl-benzylurethane, allylurethane, or to the group of allylic or vinylc ethers, whether or not substituted, or again to the group of ethylenically unsaturated amides or imides, or again to the group constituted by acrylamide and methacrylamide,

[0014] R' represents hydrogen or a hydrocarbonated radical with 1 to 40 carbon atoms, preferably 1 to 4 carbon atoms, where R' is very preferably the methyl radical,

[0015] or a blend of several monomers of formula (I),

[0016] c) and possibly of at least one other monomer chosen from among (meth)acrylic anhydride, (meth)acrylamide, or from among the (meth)acrylic esters, such as preferentially the acrylates and methacrylates with 1 to 20 carbon atoms in their ester radical, such as very preferentially the methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl or 2-ethylhexyl acrylates, the methyl or ethyl methacrylates, the hydroxylated methacrylates such as the hydroxyethyl and hydroxypropyl methacrylates, or from among the aromatic vinyl monomers such as preferentially styrene, \( \alpha-\alpha' \)-methylstyrene, styrene sulfonate, or acrylamido-2-methyl-2-propane-sulfonic acid, or from among the organophosphate monomers, such as preferentially the acrylate and methacrylate phosphates of ethylene glycol, or the acrylate and methacrylate phosphates of oxethylene and/or oxpropylene glycol, and their blends.

[0017] This grinding aid agent may be designated using the expression of a copolymer of methacrylic acid with a monomer containing an alcoxy or hydroxy polyalkylene glycol group.

[0018] The examples of the present Application show that, in comparison with a calcium carbonate which is dry ground with a diethylene glycol, a calcium carbonate according to the invention enables a cement to be obtained with a much higher degree of spreading.

[0019] This use is also characterised in that the said copolymer consists, expressed as a percentage by weight of the monomers (the sum of the percentages by weight of all the monomers equals 100%):

[0020] a) 0.5% to 50%, preferably 1% to 25%, and very preferentially 5% to 20%, of at least one anionic monomer chosen from among acrylic acid, methacrylic acid and their blends,

[0021] b) of 50% to 99.5%, preferably 75% to 99%, and very preferentially 80% to 95%, of at least one non-ionic monomer, of formula (I):

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{R}_3 \quad \text{O}_{\mu} \quad \text{O}_{\nu} \quad \text{O}_{\pi} \quad \text{O}_{\omega} \quad \text{R'}
\end{align*}
\]

[0022] where:

[0023] m, n, p and q are integers such that: m, n, p\( \leq 150 \), q\( \leq 1 \), and 5\( \leq (m+n+p)q \leq 150 \), and preferably 15\( \leq (m+n+p)q \leq 120 \),

[0024] R\(_1\) represents hydrogen or the methyl or ethyl radical,
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[0025] R₂ represents hydrogen or the methyl or ethyl radical.

[0026] R represents a radical containing an unsaturated polymerisable function, preferentially belonging to the group of vinyls, or to the group of acrylic, methacrylic, maleic esters, or to the group of unsaturated urethanes such as acrylurethane, methacrylurethane, α,ω-dimethylisopropaneyl-benzylurethane, allylurethane, or to the group of allylic or vinylic ethers, whether or not substituted, or again to the group of ethylenically unsaturated amides or imides, or again to the group constituted by acrylamide and methacrylamide.

[0027] R’ represents hydrogen or a hydrocarbonated radical with 1 to 4 carbon atoms, preferentially 1 to 4 carbon atoms, where R’ is very preferentially the methyl radical.

[0028] or a blend of several monomers of formula (l).

[0029] c) 0% to 50% of at least one other monomer chosen from among (meth)acrylic anhydride, (meth)acrylamide, or from among the (meth)acrylic esters, such as preferentially the acrylates and methacrylates with 1 to 2 carbon atoms in their ester radical, such as very preferentially the methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl or 2-ethylhexyl acrylates, the methyl or ethyl methacrylates, the hydroxylated methacrylates such as the hydroxyethyl and hydroxypropyl methacrylates, or from among the aromatic vinyl monomers such as preferentially styrene, α-methylstyrene, styrene sulfonate, or acrylamide-2-methyl-2-propane-sulfonic acid, or from among the organophosphate monomers, such as preferentially the acrylate and methacrylate phosphates of ethylene glycol, or the acrylate and methacrylate phosphates of oxethylene and/or oxpropylene glycol, and their blends.

[0030] This use is also characterised in that the said copolymer is obtained in the acidic form and possibly distilled, and is possibly partially or totally neutralised by one or more neutralisation agents having a monovalent or polyvalent cation, where the said agents are chosen preferentially from among ammonia or from among calcium, magnesium hydroxides and/or oxides, or from among sodium, potassium or lithium hydroxides, or from among the aliphatic and/or cyclic primary, secondary or tertiary amines, such as preferentially stearamylamine, the ethanolamines (mono-, di- and triethanolamine), mono- and diethyamine, cyclohexylamine, methylecyclohexylamine, amino methyl propanol, morpholine, and preferentially in that the neutralisation agent is chosen from among triethanolamine and sodium hydroxide.

[0031] This use is also characterised in that the said copolymer is obtained by processes of radical polymerisation in solution, in a direct or reverse emulsion, in suspension or precipitation in solvents, in the presence of catalytic systems and chain transfer agents, or again by processes of controlled radical polymerisation, and preferentially by nitroxide mediated polymerisation (NMP) or by cobaloximes, by atom transfer radical polymerisation (ATRP), by controlled radical polymerisation by sulphurated derivatives, chosen from among carbamates, dihydroxesters or trithiocarbonates (RAFT) or xanthates. This use is also characterised in that the said copolymer may possibly, before or after the total or partial neutralisation reaction, be treated and separated into several phases, according to static or dynamic processes known to the skilled man in the art, by one or more polar solvents belonging preferentially to the group constituted by water, methanol, ethanol, propanol, isopropanol, the butanols, acetone and tetrahydrofuran or their blends.

[0032] One of the phases then corresponds to the polymer used according to the invention.

[0033] This use is also characterised in that 0.05% to 5%, preferentially 0.1% to 3%, and very preferentially 0.1% to 1%, by dry weight of the said copolymer relative to the dry weight of calcium carbonate is used during the dry grinding of the said carbonate.

[0034] A second purpose of the invention consists of the paints obtained by the use of dry-ground calcium carbonate according to the invention.

EXAMPLES

[0035] In these examples, all the grinding operations are undertaken according to a method well known to the skilled man in the art (document FR 2 901 491 describes such a method). We shall confine ourselves here to indicating the final granulometry of the particles of calcium carbonate obtained after grinding (the skilled man in the art in reality knows how to modify the parameters of the process with a view to obtaining such a granulometry; however, one may also refer to the above-mentioned document).

[0036] In each of the tests n° 1 to 4, a matt paint is produced in aqueous phase by blending whilst stirring of the different constituents, in the proportions in grams as indicated in table 1.

<table>
<thead>
<tr>
<th>Test n°</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>292.0</td>
<td>292.0</td>
<td>292.0</td>
<td>292.0</td>
</tr>
<tr>
<td>Ammonium hydroxide (31% solution)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Coatek™ P90 (40% solution)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Mengal™ KE6N</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Byk™ 034</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>TiO2 RLO8</td>
<td>41.0</td>
<td>41.0</td>
<td>41.0</td>
<td>41.0</td>
</tr>
<tr>
<td>Omyasor™ 850/OG</td>
<td>215.0</td>
<td>215.0</td>
<td>215.0</td>
<td>215.0</td>
</tr>
<tr>
<td>CaCO3 dry ground according to test n° 1</td>
<td>328.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CaCO3 dry ground according to test n° 2</td>
<td>0</td>
<td>328.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CaCO3 dry ground according to test n° 3</td>
<td>0</td>
<td>0</td>
<td>328.0</td>
<td>0</td>
</tr>
<tr>
<td>CaCO3 dry ground according to test n° 4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>328.0</td>
</tr>
<tr>
<td>Acronal™ 290D</td>
<td>82.0</td>
<td>82.0</td>
<td>82.0</td>
<td>82.0</td>
</tr>
<tr>
<td>Monopropylene glycol</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Texanol™</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Rheo™ 3000</td>
<td>12.0</td>
<td>12.0</td>
<td>12.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Total (g) | 1000.0 | 1000.0 | 1000.0 | 1000.0 |

Coatek™ P90 designates a thickener sold by the company COATEX™. 
Rheo™ 3000 designates a thickener sold by the company COATEX™. 
Mengal™ KE6N designates a bactericide sold by the company TRIOY™. 
Byk™ 034 designates an anti-foaming agent sold by the company BYK™. 
TiO2 RLO8 designates a titanium dioxide powder sold by the company MIL- LENAUM™. 
Omyasor™ 850/OG designates a calcium carbonate sold by the company OMYA™. 
Acronal™ 290D designates a binder sold by the company BASF™. 
Texanol™ designates a coalescence agent sold by the company EAST-MANN™

Test No. 1

[0037] This test illustrates the prior art and uses a calcium carbonate obtained by dry grinding in the presence of 3000
ppm (relative to the dry weight of calcium carbonate) of a grinding agent of the prior art, which is diethylene glycol.  

[0038] After grinding a calcium carbonate is obtained, 73.8% and 48.5% by weight of the particles of which have an average diameter lower respectively than 2 μm and 1 μm (as measured using a Sedigraph™ 5100).

Test No. 2

[0039] This test illustrates the prior art and uses a calcium carbonate obtained by dry grinding in the presence of 3000 ppm (relative to the dry weight of calcium carbonate) of a grinding agent of the prior art which is a polymer consisting, by weight percentage, 81.5% of methoxy polyethylene glycol methacrylate of molecular weight 2000, 4.9% of methacrylic acid, and 13.6% of acrylic acid.

[0040] After grinding a calcium carbonate is obtained, 74.5% and 44.1% by weight of the particles of which have an average diameter lower respectively than 2 μm and 1 μm (as measured using a Sedigraph™ 5100).

Test No. 3

[0041] This test illustrates the prior art and uses a calcium carbonate obtained by dry grinding in the presence of 1400 ppm (relative to the dry weight of calcium carbonate) of a grinding agent of the prior art, which is diethylene glycol.  

[0042] After grinding a calcium carbonate is obtained, 47.1% and 30.00% by weight of the particles of which have an average diameter lower respectively than 2 μm and 1 μm (as measured using a Sedigraph™ 5100).

Test No. 4

[0043] This test illustrates the prior art and uses a calcium carbonate obtained by dry grinding in the presence of 1400 ppm (relative to the dry weight of calcium carbonate) of a grinding agent of the prior art which is a polymer consisting, by weight percentage, 81.5% of methoxy polyethylene glycol methacrylate of molecular weight 2000, 4.9% of methacrylic acid, and 13.6% of acrylic acid.

[0044] After grinding a calcium carbonate is obtained, 45.4% and 28.0% by weight of the particles of which have an average diameter lower respectively than 2 μm and 1 μm (as measured using a Sedigraph™ 5100).

[0045] The polymer used in tests n° 2 and 4 is obtained by polymerisation techniques well known to the skilled man in the art.

[0046] In a first beaker the following are introduced at ambient temperature and whilst stirring: 259.02 of methoxy polyethylene glycol methacrylate of molecular weight equal to 2000 g/mol, a solution containing 15.36 g of methacrylic acid and 274.39 g of water, a solution containing 69.86 g of untreated water and 50.25 g of acrylic acid.  

[0047] In a second beaker the following are introduced at ambient temperature and whilst stirring: 2.38 g of thiolactic acid (of 98.5% mass purity) and 52.14 g of water.  

[0048] In a third beaker the following are introduced at ambient temperature and whilst stirring: 2.84 g of ammonium persulphate (NH₄)₂S₂O₈ and 51.90 g of water.  

[0049] In a fourth beaker the following are introduced at ambient temperature and whilst stirring: 0.56 g of ammonium persulphate (NH₄)₂S₂O₈ and 10.87 g of water.

[0050] In a single-casing cylindrical reactor, surmounted by a refrigerating column, by an anchor stirring system and 3 inlets, 351.39 g of water and 295.61 g of isopropanol are introduced. The reactive medium is heated whilst stirring (230 rpm) to 84±2°C. The contents of the first 3 beakers are introduced into the reactive medium in 2 hours. The introduction nozzles are then rinsed with 20.84 g of water (this water goes directly into the reactive medium). The solution of the 4th beaker is then added to the reactive medium, and the blend is fired for 1 hour at 84±2°C (at 230 rpm). At the end of the reaction the device is rinsed with 52.13 g of water. The temperature is then raised and 604.78 g of distilled water and 69.34 g of sodium hydroxide at 50% mass in water is added to the reactive medium. Finally the medium is diluted with 20.85 g of water. It is cooled again before obtaining the polymer of the invention.

[0051] For each of the tests n° 1 to 4, the Stormer™, ICT™ and Brookfield™ viscosities were determined according to the methods well known to the skilled man in the art. Certain optical characteristics of the paints obtained were also measured, such as notably L whiteness, the "3 Hunterlab filters' Sub-tone", covering power or contrast ratio, and the level of brightness at angles equal to 60° and 85°.

[0052] The methods used are notably described in document FR 2 872 815.

[0053] The results are shown in tables 2 and 3.

### TABLE 2

<table>
<thead>
<tr>
<th>Viscosities</th>
<th>Test n°1</th>
<th>Test n°2</th>
<th>Test n°3</th>
<th>Test n°4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time t = 0</td>
<td>µ (P)</td>
<td>1.9</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>µ (K - U)</td>
<td>102</td>
<td>106</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>µ (10 rpm, mPa·s)</td>
<td>13700</td>
<td>15100</td>
<td>11600</td>
</tr>
<tr>
<td>Instant t =</td>
<td>µ (100 mPa·s)</td>
<td>3300</td>
<td>3600</td>
<td>2900</td>
</tr>
<tr>
<td>1 month 50°C.</td>
<td>µ (10 mPa·s)</td>
<td>18900</td>
<td>18400</td>
<td>12700</td>
</tr>
<tr>
<td></td>
<td>µ (100 mPa·s)</td>
<td>4900</td>
<td>4750</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>µ (100 mPa·s)</td>
<td>43900</td>
<td>32100</td>
<td>15400</td>
</tr>
<tr>
<td></td>
<td>µ (100 mPa·s)</td>
<td>14000</td>
<td>8340</td>
<td>4500</td>
</tr>
<tr>
<td></td>
<td>µ (100 mPa·s)</td>
<td>12000</td>
<td>4700</td>
<td>3400</td>
</tr>
</tbody>
</table>

### TABLE 3

<table>
<thead>
<tr>
<th>Test n°</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement of the &quot;L&quot;</td>
<td>99.2</td>
<td>99.1</td>
<td>98.7</td>
<td>98.6</td>
</tr>
<tr>
<td>&quot;3 Hunterlab filters' Sub-tone&quot;</td>
<td>2.2</td>
<td>2.3</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Covering power of dry film</td>
<td>96.9%</td>
<td>96.8%</td>
<td>96.0%</td>
<td>95.9%</td>
</tr>
<tr>
<td>Contrast ratio</td>
<td>60°</td>
<td>4.7</td>
<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td>Level of brightness</td>
<td>85°</td>
<td>32.9</td>
<td>33.5</td>
<td>14.9</td>
</tr>
</tbody>
</table>

[0054] By comparing the tests 2 by 2 (1 to 2, and 3 to 4), it is observed that the optical properties of the paint films are in the context of the invention at the same level as for the prior art.
Conversely, a clear drift of the Brookfield® viscosity is observed in the case of paints formulated according to the prior art. At the same time, this viscosity remains much more stable in the context of the invention.

We have therefore succeeded in developing a dry-ground calcium carbonate which, in the paint field, has a more stable Brookfield viscosity, without modifying the optical properties of the dry film.

1. A calcium carbonate for use in a paint which is dry-ground in the presence of a copolymer grinding aid agent comprising:
   a) at least one anionic monomer chosen from acrylic acid, methacrylic acid and their blends,
   b) at least one non-ionic monomer, of formula (I):

   \[
   R - O - R_1 - O - R_2 - O - R_3
   \]

   where:
   - \( m, n, p \) and \( q \) are integers such that: \( m, n, p \leq 150, q \geq 1 \)
   - \( 5 \leq (m+n+p)q \leq 150 \)
   - \( R \) represents hydrogen or the methyl or ethyl radical,
   - \( R_1 \) represents hydrogen or the methyl or ethyl radical,
   - \( R_2 \) represents hydrogen or the methyl or ethyl radical,
   - \( R_3 \) represents a radical containing an unsaturated polymerisable function chosen from the group of vinyls, the group of acrylic, methacrylic, and maleic esters, the group of unsaturated urethanes selected from the group consisting of acrylurethane, methacrylurethane, and allylurethane, the group of allylic or vinyllic ethers, whether or not substituted, the group of ethylenically unsaturated amides or imides, and the group consisting of acrylamide and methacrylamide, and
   - \( R' \) represents hydrogen or a hydrocarbonated radical with 1 to 40 carbon atoms,
   - or a blend of several monomers of formula (I),
   - c) and optionally at least one other monomer chosen from (meth)acrylic anhydride and (meth)acrylamide, the esters chosen from the acrylates and methacrylates with 1 to 20 carbon atoms in their ester radical, and the hydroxylated methacrylates chosen from the hydroxyethyl and hydroxypropyl methacrylates, the aromatic vinyl monomers chosen from styrene, \( \alpha \)-methylstyr- ene, and styrene sulfonate, and acrylamido-2-methyl-2-propane-sulfonic acid, the organophosphate monomers chosen from the acrylate and methacrylate phosphates of ethylene glycol, and the acrylate and methacrylate phosphates of oxyethylene and/or oxypoly-ylene glycol, and their blends.

2. The calcium carbonate according to claim 1, wherein said copolymer comprises, expressed as a percentage by weight of the monomers in which the sum of the percentages by weight of all the monomers equals 100%:
   a) 0.5% to 50% of at least one anionic monomer chosen from acrylic acid, methacrylic acid and their blends,
   b) 50% to 99.5%, of at least one non-ionic monomer, of formula (I):

   \[
   R - O - R_1 - O - R_2 - O - R_3
   \]

   where:
   - \( m, n, p \) and \( q \) are integers such that: \( m, n, p \leq 150, q \geq 1 \)
   - \( 5 \leq (m+n+p)q \leq 150 \)
   - \( R \) represents hydrogen or the methyl or ethyl radical,
   - \( R_1 \) represents hydrogen or the methyl or ethyl radical,
   - \( R_2 \) represents hydrogen or the methyl or ethyl radical,
   - \( R_3 \) represents a radical containing an unsaturated polymerisable function chosen from the group of vinyls, the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters, the group of unsaturated urethanes selected from the group consisting of acrylurethane, methacrylurethane, \( \alpha \)-ct dimethyl-isopropanol-benzyletherate, and allylurethane, the group of allylic and vinyllic ethers, whether or not substituted, the group of ethylenically unsaturated amides or imides, and the group consisting of acrylamide and methacrylamide,
   - or a blend of several monomers of formula (I), and
   - c) 0% to 50% of at least one other monomer chosen from (meth)acrylic anhydride and (meth)acrylamide, the esters chosen from the acrylates and methacrylates with 1 to 20 carbon atoms in their ester radical, and the hydroxylated methacrylates chosen from the hydroxyethyl and hydroxypropyl methacrylates, the aromatic vinyl monomers chosen from styrene, \( \alpha \)-methylstyrene, and styrene sulfonate, and acrylamido-2-methyl-2-propane-sulfonic acid, the organophosphate monomers chosen from the acrylate and methacrylate phosphates of ethylene glycol, and the acrylate and methacrylate phosphates of oxyethylene and/or oxypoly-ylene glycol, and their blends.

3. The calcium carbonate according to claim 1, wherein said copolymer is obtained in the acidic form and optionally distilled, and is optionally partially or totally neutralised by one or more neutralisation agents having a monovalent or polyvalent cation, where said agents are chosen from monochloroquine and calcium and magnesium hydroxides and/or oxides, sodium, potassium and lithium hydroxides, and the aliphatic and/or cyclic primary, secondary or tertiary amines chosen from stearylamine, the ethanolamines, mono- and diethy- lamine, cyclohexylamine, methylethylhexylamine, amino methyl propanol, and morpholine.

4. The calcium carbonate according to claim 1, wherein said copolymer is obtained by a polymerisation process chosen from of radical polymerisation in solution, in a direct or reverse emulsion, in suspension or precipitation in solvents, in the presence of cationic systems and chain transfer agents, or a process of controlled radical polymerisation, chosen from nitroxide mediated polymerisation (NMP) or cobraoximes, atom transfer radical polymerisation (ATRP), and controlled radical polymerisation by sulphurated derivatives, chosen from carbamates, dithiocesters or trithiocarbonates (RAFT) or xanthates.

5. The calcium carbonate according to claim 3, wherein said copolymer is, before or after the total or partial neutralisation reaction, treated and separated into several phases,
according to static or dynamic processes, by one or more polar solvents selected from the group consisting of water, methanol, ethanol, propanol, isopropanol, the butanols, acetone, tetrahydrofuran and their blends.

6. The calcium carbonate according to claim 1, wherein 0.05% to 5% by dry weight of the said copolymer relative to

the dry weight of calcium carbonate is used during the dry grinding of the said carbonate.

7. A paint obtained by use of the dry-ground calcium carbonate according to claim 1.

* * * * *