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1215 1396.4 17 January 2012 (17.01.2012) EP(71) Applicant (for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PA, PG, QA, RW, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, 3013 AL Rotterdam (NL).(71) Applicant (for AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, 100 Victoria Embankment, London Greater London EC4Y0DY (GB).(71) Applicant (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Unilever house, B.D. Sawant Marg Chakala Andheri (East) 400 099 Mumbai, Maharashtra (IN).

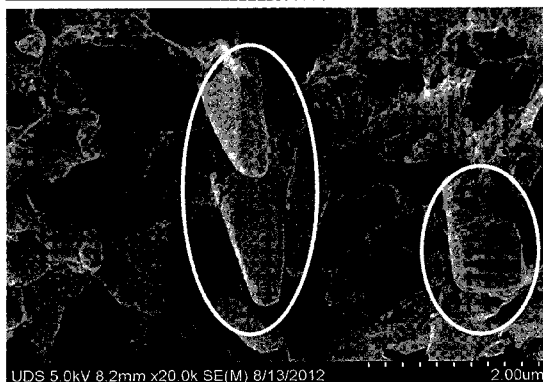
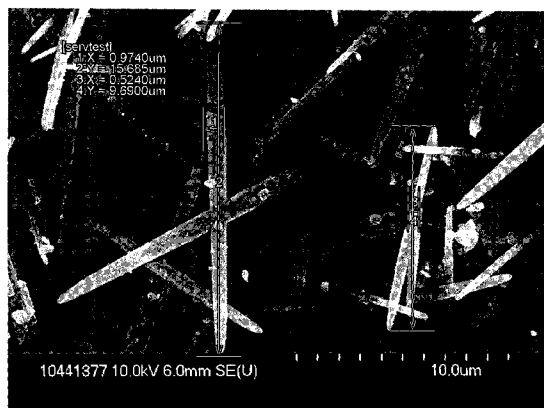
(72) Inventors; and

(71) Applicants (for US only): **ASHCROFT, Alexander Thomas** [GB/GB]; Unilever R&D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **CAO, Jian** [CN/GB]; Unilever R&D Colworth, Sharnbrook, Bedfordshire MK44 1LQ (GB). **FAWCETT, Vicky Marie** [GB/GB]; Unilever R&D Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **MA, Shouwei** [CN/CN]; Room 601, Lane 112, 399 Chuang Xin Zhong Road, Pudong, Shanghai 201210 (CN). **PELAN, Edward George** [GB/NL]; Unilever R&D

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(54) Title: LIQUID COMPOSITION FOR CLEANING OF HEAD SURFACES

Figure 1



(57) Abstract: A liquid composition for cleaning of hard surfaces is provided. The composition combines good abrasive strength with little damage to the surface to be cleaned. The liquid composition comprises surfactant, and a particulate calcium carbonate abrasive composed of acicular particles at a concentration from 2 to 40% based on the total weight of the composition.



Vlaardingen B.V., Olivier van Noortlaan 120, 3133 AT Vlaardingen (NL). **STOYANOV, Simeon Dobrev** [BG/NL]; Unilever R&D Vlaardingen B.V., Olivier van Noortlaan 120, 3133 AT Vlaardingen (NL). **ZHOU, Weizheng** [CN/CN]; Unilever (China) Investing Company, 66 LinXin Road, Linkong Economic Development Zone, Changning District, Shanghai 200335 (CN). **ZHOU, Huan-Jun** [CN/CN]; Unilever (China) Investing Company, 66 LinXin Road, Linkong Economic Development Zone, Changning District, Shanghai 200335 (CN).

(74) **Agent: CHINA PATENT AGENT (HK)LTD.**; 22/F., Great Eagle Center, 23 Harbour Road, Wanchai, Hong Kong (CN).

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LIQUID COMPOSITION FOR CLEANING OF HARD SURFACES

The present invention relates to a cleaning composition for hard surfaces for household use, and to a method for cleaning hard surfaces using the composition.

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BACKGROUND OF THE INVENTION

Cleaning liquids for household surfaces (e.g. tables, kitchen, bathroom) are well known. These liquids often contain ingredients that have the purpose to facilitate the easy removal of stains and soils from hard surfaces while abrasion and scratching of the surface should be as low as possible. Calcium carbonate is often used as an abrasive in such cleaning liquids, and tough soil on surfaces may be removed via these liquid abrasive cleaners. Calcium carbonate (CaCO_3) of known particle size, in the calcite crystal form, is used as the abrasive in current commercially available liquid abrasive cleaners. This abrasive is a highly effective tough soil remover, but with this presents the unavoidable potential for surface damage when cleaning. Increasing the level of calcite in the formulation improves cleaning, but also increases surface damage.

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EP 0 103 325 A 1 discloses a liquid scouring cleaning composition comprising an abrasive powder, for example precipitated calcium carbonate (aragonite).

Aragonite is one of the naturally occurring crystal forms of calcium carbonate (CaCO_3). Aragonite can exist in three crystal habits: acicular pyramidal, tabular, and pseudo-hexagonal (Kirk Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 4, John Wiley and Sons, New York, p. 796). Acicular crystal habit leads to needle-like shape, tabular crystal habit leads to a tablet structure, and pseudo-hexagonal crystal habit leads to a hexagonal appearance.

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US 5,164,172 discloses a process for producing aragonite crystal form calcium carbonate with acicular shape, which has a particle size of 10 to 100 micrometer by 0.5 to 4.0 micrometer.

30

US 2003/0180208 A 1 discloses a process for preparation of precipitated aragonite, having a needle-like shape ('acicular aragonite'), with a thickness of a micron or less. The precipitated aragonite can be used in applications in the prior art in which regular calcium carbonate is used.

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JP 2002-180090 A discloses a silica-based compound consisting of an aggregate of acicular crystals, plate crystals or columnar crystals and having an average aggregate particle diameter of 0.5-500 micrometer.

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WO 2009/040597 discloses a cleaning composition for hard surfaces, containing solid inorganic nanoparticles having a particle size of from 0.5 to 5 micrometer, a surface area of from 10 to 50 m²/g and a crystallinity degree lower than 50 percent. The inorganic nanoparticles may be carbonates, and in one of the examples carbonate-substituted non-stoichiometric hydroxyapatite is used. These particles have the advantage that the abrasiveness has decreased.

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US 2010/0263693 A1 discloses hard surface treatment compositions, wherein the particle size of an abrasive agent ranges from about 1 to 1000 micrometer, more preferably from about 10 to 100 micrometer. Abrasive agents that will not scratch glass or ceramic surfaces are preferred, and these include calcium carbonate, siliceous chalk, diatomaceous earth, colloidal silicon dioxide, sodium metasilicate, talc, and organic abrasive materials.

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WO 2011/087733 A1 discloses a liquid cleaning composition comprising abrasive particles which have been defined based on roughness and hardness. The abrasive particles preferably comprise polymeric particles, e.g. polyurethane.

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25 SUMMARY OF THE INVENTION

The calcium carbonate forms used nowadays have the disadvantage that they contribute to the scratching of hard surfaces. Hence it is an objective of the present invention to provide a composition for cleaning of hard surfaces that facilitates the easy removal of soil, while minimising scratching and abrasion of the surface.

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We have now found that this objective can be met by replacing at least part of the conventional ground calcium carbonate (in calcite crystal form) with particulates of precipitated calcium carbonate, wherein the precipitated calcium carbonate has an acicular morphology. When the acicular precipitated calcium carbonate is introduced into liquid abrasive cleaning composition, either totally or partially replacing the

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conventional ground calcium carbonate, there is a reduced damage profile on hard surfaces. A damaged surface may even be repaired or polished when the composition of the invention is used.

5 Hence in a first aspect the present invention provides a liquid composition for cleaning of hard surfaces, comprising surfactant, and a particulate calcium carbonate abrasive composed of primary particles which are acicular and which have a length of 2 micrometer or more, in which the level of the particulates ranges from 2 to 40% based on the total weight of the composition.

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In a second aspect the present invention provides a method for cleaning of a hard surface, wherein a composition according to the first aspect of the invention is used.

15 DETAILED DESCRIPTION

The technical and scientific terms herein have their common meaning as understood by the skilled person, unless stated otherwise.

20 All percentages, unless otherwise stated, refer to the percentage by weight. The abbreviation 'wt%' or '% (w/w)' refers to percentage by weight.

In case a range is given, the given range includes the mentioned endpoints.

25 In the context of the present invention, the expressions 'soil' and 'stain' generally comprise all kinds of soils and stains generally encountered in the household, either of organic or inorganic origin, whether visible or invisible to the naked eye, including soiling solid debris and/or with bacteria or other pathogens.

30 In the context of the present invention, a liquid composition refers to a composition that will flow under the force of gravity. This is in contradiction of pastes or gels, which keep their shape under the force of gravity.

Calcium Carbonate

35 The use of calcium carbonate in liquid hard surface cleaners is well known. The most common sources of calcium carbonate (CaCO_3) are rocks like limestone, chalk, marble,

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and travertine. The rock can be grinded into small or big pieces containing calcium carbonate. Calcium carbonate can also be made and purified by a precipitation process. Precipitated calcium carbonate is usually produced by a series of chemical reactions. First step is conversion of limestone into calcium oxide and carbon dioxide by means of
5 calcination at temperatures in excess of 900°C. Second step is slaking, wherein the calcium oxide reacts with water, resulting into calcium hydroxide. In the third step (precipitation), the resulting milk of lime is purified and carbonized with the carbon dioxide obtained from the calcination process, and calcium carbonate precipitates. This precipitate may be concentrated by filtration, and the filter cake is then dried and
10 subsequently disagglomerated in grinders. The particle size, as well as the crystal form, is controlled by temperature, concentration of reactants and time.

Calcium carbonate may occur naturally or may be synthetically produced in three particular crystalline morphologies, calcite, aragonite, and less commonly found,
15 vaterite. The vaterite form of calcium carbonate is metastable and irreversibly transforms into calcite and aragonite. There are many different polymorphs (crystal habits) for each of these crystalline forms. The calcite crystalline morphology is the most commonly used crystal form of calcium carbonate. Over 300 crystalline forms of calcite have been reported in the literature.

20 The composition of the invention comprises a particulate calcium carbonate abrasive composed of primary particles which are acicular and which have a length of 2 micrometer or more. By 'primary particles' is meant individual particles. For the purposes of the present invention, the primary particles of the particulate calcium
25 carbonate abrasive are acicular and have a length of 2 microns or greater. The primary particles may associate under certain conditions to form larger secondary structures such as aggregates or agglomerates.

For the purposes of the present invention, preferably the calcium carbonate abrasive
30 comprises a crystalline calcium carbonate in which the crystals are acicular with a largest dimension of 2 micrometer or more. The term 'crystal' means an essentially fully dense solid composed of atoms arranged in an orderly repetitive array bounded by plane surfaces which are the external expression of internal structure.

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The term 'acicular' in this context refers to the shape of the crystals. Usually, crystals grow in three directions, length, width and height. Some crystals however, have one or two preferred growth directions. Acicular crystals have a preferred crystal growth in one direction. Examples are crystals in the form of needles, rods, fibres, whiskers or
5 columns and the like. For the purposes of the present invention, preferred acicular crystals are rod-like or needle-like with a generally uniform, typically generally circular, cross-sectional shape. Alternatively, the cross-sectional shape may be not completely circular, but may have a polygonal shape, preferably a convex polygonal shape, for example a hexagonal shape. The polygonal shape may be irregular, which means that
10 the sides of such a polygonal shape may have different lengths. Alternatively, the cross-sectional shape may be ellipsoidal.

Acicular crystalline forms of calcium carbonate are available naturally, or may be produced by precipitation production technology.

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A specific class of material suitable for use in the invention includes aragonite crystal form calcium carbonates such as those described for example in US 5,164,172. According to US 5,164,172, aragonite crystal form calcium carbonate with an acicular shape is prepared by premixing aragonite calcium carbonate and $\text{Ca}(\text{OH})_2$ to prepare
20 an aqueous slurry, adding a water-soluble phosphoric acid compound (such as phosphoric acid or a water-soluble salt thereof) into the aqueous slurry, and introducing CO_2 gas into the aqueous slurry to cause a carbonation reaction to take place. In this process, the molar ratio of the aragonite calcium carbonate to $\text{Ca}(\text{OH})_2$ slurry is preferably 1:7 to 1:5000. The resulting aragonite calcium carbonate crystals have an
25 acicular shape and have a particle size of 10 to 100 micrometer (length) by 0.5 to 4.0 micrometer (width). The crystals are shown by microscopy to be rod-like or needle-like with a length of 10 to 100 microns. The rods or needles are generally uniform and typically circular in cross-section, with a cross-sectional diameter of 0.5 to 4.0 micrometer. Alternatively, the cross-section shape may be not circular, but may
30 have a polygonal shape, preferably a convex polygonal shape, for example a hexagonal shape. The polygonal shape may be irregular, which means that the sides of such a polygonal shape may have different lengths. Alternatively, the cross-sectional shape may be ellipsoidal. Suitable aragonite crystal form calcium carbonates for use in the invention are commercially available and include those marketed by Maruo Calcium
35 Company Limited, Japan under the trade name Whiscal®.

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Hence, preferably, the crystals are acicular aragonite with a length ranging from 2 to 100 micrometer, preferably from 5 to 100 micrometer, preferably from 10 to 100 micrometer, preferably from 10 to 50 micrometer. Most preferred the length of the
5 crystal ranges from 10 to 30 micrometer.

Preferably the crystals are acicular aragonite with a width ranging from 0.1 to 4.0 micrometer, preferably 0.1 to 2.0 micrometer, preferably from 0.1 to 1.0 micrometer. More preferred the width of the crystals ranges from 0.3 to 1.0 micrometer, more
10 preferred from 0.5 to 1.0 micrometer. Least damage to a hard surface is obtained by crystals which have an average width according to these preferred ranges.

Preferably a non-circular cross-sectional shape, preferably a polygonal shape, preferably a convex polygonal shape, for example a hexagonal shape, or preferably an
15 ellipsoidal shape, can be enclosed by a minimum bounding circle with a diameter ranging from 0.1 to 4.0 micrometer. The diameter of the minimum bounding circle can be considered to be the cross-sectional diameter of the rod or needle, in this case. More preferred the diameter of such bounding circle ranges from 0.1 to 2.0 micrometer, preferably from 0.1 to 1.0 micrometer, more preferred from 0.3 to 1.0 micrometer, and
20 even more preferred from 0.5 to 1.0 micrometer.

The ratio between the length and the width of a crystal, the so-called aspect ratio, is higher than 1 for acicular crystals. The higher the aspect ratio, the longer the crystal relative to the width. For the purposes of the present invention the aspect ratio is
25 preferably at least 2.5, more preferably at least 10. Preferably the crystals are acicular aragonite with an aspect ratio ranging from 2.5 to 1000, preferably from 2.5 to 200, preferably from 10 to 100, and more preferably ranges from 10 to 60, and most preferably from 20 to 30.

30 For the purposes of the present invention, the most preferred aragonite calcium carbonate crystals are rod-like or needle-like as described above, with a length ranging from 10 to 30 micrometer, a width ranging from 0.5 to 1.0 micrometer and an aspect ratio ranging from 20 to 30.

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In case the cross-sectional shape of a crystal is not circular, then preferably the ratio between the longest and shortest dimensions of the cross-sectional shape, ranges from 1 : 0.2 to 1 : 1, more preferably from 1 : 0.3 to 1 : 0.9, more preferred from 1 : 0.5 to 1 : 0.8.

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Although aragonite has a higher Moh's hardness than calcite (3.5 to 4 for aragonite, versus 3 for calcite), the damage of the aragonite acicular crystals to hard surfaces is less than calcite. The particulate calcium carbonate abrasive of the invention even may lead to repair or polishing of a damaged hard surface, in particular a plastic hard

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Crystal morphology and structure may be determined by standard techniques known to those skilled in the art such as scanning electron microscopy (SEM). SEM is an imaging and analysis technique based on the detection of electrons and X-rays that are emitted from a material when irradiated by a scanning electron beam. Imaging allows the user to distinguish between primary particle and agglomerate sizes.

15

Automated image analysis using computer software enables the user to determine particle size distributions. Scanning electron microscopy (SEM) is a particle counting technique and produces a number-weighted size distribution. Accordingly the figures quoted herein for particle length and width will generally represent average values over a population of particles, more specifically the D[1,0] number-length mean of the particle length or the particle width respectively.

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Mixtures of any of the above described materials may also be used.

25

The concentration of the particulate calcium carbonate abrasive ranges from 2 to 40% based on the total weight of the composition. Preferably, the concentration of calcium carbonate abrasive ranges from 5 to 30%, preferably from 8 to 25%, preferably from 10 to 25%, preferably from 15 to 20%, based on the total weight of the composition.

30

Preferably, the composition further comprises phosphate ions and/or halophosphate ions, preferably phosphate ions and/or fluorophosphate ions. Phosphate ions (PO_4^{3-}) or halophosphate ions (PO_3X^{2-} , wherein X is Br, Cl, F, or I) have the advantage that when added to the composition, that the dynamic viscosity of the composition is reduced as

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compared to a composition without these added phosphate ions. Preferably the halophosphate ion is fluorophosphate (PO_3F^{2-}). Also combinations of phosphate ions and halophosphate ions are possible. These ions may be added to the composition in the form of their sodium salt, or any other common counterion.

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The use of these phosphate ions and/or halophosphate ions leads to easier dosing of the composition, or even the possibility to spray the cleaning composition, while still having a good abrasive power. Usually the presence of high concentrations of calcium carbonate will lead to thick, highly viscous compositions that may be difficult to dose.

10 By the presence of phosphate ions and/or halophosphate ions in combination with the calcium carbonate abrasive, the amount of calcium carbonate abrasive can be increased to increase the abrasive strength of the composition, while the viscosity of the composition is not increased (which would make it more difficult to handle).

15 Preferably, the weight ratio between calcium carbonate abrasive and phosphate ions and/or halophosphate ions ranges from 200:1 to 10:1, preferably from 100:1 to 15:1, preferably from 80:1 to 20:1. Preferably, the weight ratio ranges even more preferred from 50:1 to 25:1.

20 Preferably the composition only contains the calcium carbonate abrasive of the invention as abrasive material. Alternatively, the calcium carbonate abrasive of the invention may be used in combination with other calcium carbonate abrasives, as known from the prior art. In that case the total concentration of calcium carbonate abrasives preferably ranges from 15 to 40% by weight of the composition, preferably
25 from 18 to 30% by weight, preferably from 20 to 25% by weight of the composition. The composition of the invention preferably comprises ground calcium carbonate in the form of calcite crystals. The most commonly used calcium carbonate abrasive in the compositions of the prior art is calcium carbonate in the form of calcite, that is obtained by grinding natural calcium carbonate. Preferably, this ground calcium carbonate in the
30 form of calcite crystals have a largest dimension ranging from 20 micrometer to 100 micrometer, preferably from 20 micrometer to 70 micrometer, and a ratio between largest and smallest dimension ranging from 1 to 5, preferably from 1 to 3. More preferred the circularity of the ground calcium carbonate is relatively high, hence the ratio between largest and smallest dimension preferably ranges from 1 to 2. If this
35 ground calcium carbonate is present in the composition of the invention, then

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preferably the amount of particulate calcium carbonate abrasive composed of primary particles which are acicular is at least 50 wt% of the total amount of calcium carbonate, preferably at least 75 wt%. Hence preferably at least half or even most of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention.

- 5 More preferred at least 75% of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention.

- Additionally the composition of the invention may comprise other particulates calcium carbonate, in addition to the calcium carbonate abrasive of the invention. Hence,
- 10 preferably the composition further comprises particulate precipitated calcium carbonate with a calcite crystal structure, having a largest dimension ranging from 0.1 to 10 micrometer, preferably from 0.2 to 6 micrometer, preferably from 0.4 to 4 micrometer, and a ratio between largest and smallest dimension ranging from 1 to 10, preferably from 1 to 5. More preferred the circularity of the particulate precipitated
- 15 calcium carbonate with a calcite crystal structure is relatively high, hence the ratio between largest and smallest dimension preferably ranges from 1 to 3, more preferably from 1 to 2. Preferably at least half or even most of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention. More preferred at least 75% of the calcium carbonate present is in the form of the acicular calcium carbonate of the
- 20 invention.

- Preferably, precipitated calcium carbonate with a calcite crystal structure is obtained by a process involving the subsequent steps of calcination of calcium carbonate to calcium oxide and carbon dioxide; slaking of calcium oxide with water to calcium
- 25 hydroxide; and reacting calcium hydroxide with carbon dioxide to yield particulates of precipitated calcium carbonate and water; and optionally concentrating the precipitated calcium carbonate.

- In a preferred embodiment, the particulate precipitated calcium carbonate with a calcite
- 30 crystal structure comprises a crystal having a calcite prismatic crystal structure. Preferably, the particulate precipitated calcium carbonate with a calcite crystal structure has a prismatic crystal structure, with a largest dimension ranging from 0.1 to 2 micrometer, preferably from 0.2 to 1 micrometer. Preferably, the particle size distribution is such that at least 50% of the particles has a size smaller than
- 35 3 micrometer, preferably smaller than 2 micrometer, preferably smaller than

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1 micrometer. Preferably at least 90% of the particles has a size smaller than 6 micrometer. These dimensions relate to the primary particles, that may agglomerate in clusters. A preferred example of this precipitated calcium carbonate is ViCALity ALBAFIL® PCC supplied by Speciality Minerals Inc. (Bethlehem, PA, USA). Preferably
5 at least half or even most of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention. More preferred at least 75% of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention.

In another preferred embodiment the particulate precipitated calcium carbonate with a
10 calcite crystal structure comprises a crystal having a calcite scalenohedral crystal structure. Preferably the particulate precipitated calcium carbonate with a calcite crystal structure has a scalenohedral crystal structure, and wherein the crystals are agglomerated, and wherein the agglomerate has a largest dimension ranging from 1 to 20 micrometer, preferably from 2 to 15 micrometer. Preferably, the particle size
15 distribution is such that at least 50% of the particles has a size smaller than 3 micrometer, preferably smaller than 2 micrometer, preferably smaller than 1 micrometer. Preferably at least 90% of the particles has a size smaller than 6 micrometer. Alternatively, the primary particles from which the agglomerates are made, preferably have a largest dimension of maximally 1 micrometer. Preferably at least half
20 or even most of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention. More preferred at least 75% of the calcium carbonate present is in the form of the acicular calcium carbonate of the invention.

Also combinations of various forms precipitated calcium carbonate with a calcite crystal
25 structure are preferably used. For example, the composition of the invention may contain in addition to the abrasive acicular calcium carbonate, a combination of precipitated calcium carbonate with a calcite prismatic crystal structure and precipitated calcium carbonate having a calcite scalenohedral crystal structure. Preferably, if both forms are present, the weight ratio of the two forms ranges from 5:1 to 1:5.

30 If one or more of precipitated calcium carbonate with a calcite prismatic crystal structure is present, then preferably at least 30%, more preferably at least 50% or even at least 75% by weight of total amount of calcium carbonate, is in the form of particulate calcium carbonate abrasive composed of primary particles which are
35 acicular and which have a length of 2 micrometer or more.

Surfactants

The liquid cleaning composition of the invention comprises a surfactant, preferably at a concentration of maximally 50% by weight of the composition. The surfactant (detergent active) is generally chosen from anionic and nonionic detergent actives. The cleaning composition may further comprise cationic, amphoteric and zwitterionic surfactants. Preferably, the total amount of surfactant the cleaning composition is at least 0.1%, more preferably at least 0.5%. The maximum amount is usually less than 30%, more preferably not more than 20%, or even at or below 10% by weight.

Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphononic acids which have in the molecular structure a branched or straight chain alkyl group containing from 6 to 22 carbon atoms in the alkyl part. Examples of such anionic surfactants are water soluble salts of:

- (primary) long chain (e.g. 6-22 C-atoms) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
 - alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
 - secondary alkanesulphonates;
- and mixtures thereof.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
 - fatty acid monoglyceride sulphates;
 - sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups;
 - alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
 - the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali,
- and mixtures thereof.

The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as

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sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulphonates and mixtures with olefinsulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

- 5 The most preferred anionic surfactants are alkyl-aromatic sulphonates such as alkylbenzenesulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of alkylbenzenesulphonates or of alkyl-toluene-, -xylene- or -phenolsulphonates, alkyl-naphthalene-sulphonates, ammonium diaminonaphthalene-sulphonate, and sodium
10 dinonyl-naphthalene-sulphonate.

If synthetic anionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be at least 0.1%, preferably at least 0.5%, more preferably at least 1.0%, but not more than 20%, preferably at most 15%, more
15 preferably at most 10%.

A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive
20 hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB. Particular examples include:

- 25
- the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
 - condensates of alkylphenols having C₆-C₁₅ alkyl groups with 5 to 25 moles of
30 ethylene oxide per mole of alkylphenol;
 - condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

35 Other classes of nonionic surfactants are:

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- tertiary amine oxides of structure $R^1R^2R^3N-O$, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure $R^1R^2R^3P-O$, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulphoxides of structure $R^1R^2S=O$, where R^1 is an alkyl group of from 10 to 18 carbon atoms and R^2 is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- fatty acid alkylolamides, such as the ethanol amides;
- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans.

The concentration of the nonionic surfactant preferably employed in the cleaning composition of the invention will preferably be at least 0.1%, more preferably at least 0.5%, most preferably at least 1%. The amount is suitably at most 20%, preferably not more than 15% and most preferably not more than 10%.

It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in said compositions. Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

Examples of suitable zwitterionic surfactants can be found among derivatives of

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aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance betaine and betaine derivatives such as alkyl betaine, in particular C₁₂-C₁₈ alkyl betaine, 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine, 3-(cetyl-methyl-phosphonium)-propane-1-sulphonate betaine and N,N-dimethyl-N-dodecyl-glycine. Other well known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.

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Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks: 'Surface Active Agents' Vol.1, by Schwartz & Perry, Interscience 1949; 'Surface Active Agents' Vol.2 by Schwartz, Perry & Berch, Interscience 1958; the current edition of 'McCutcheon's Emulsifiers and Detergents' published by Manufacturing Confectioners Company; Tenside-Taschenbuch', H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

15

The pH of the composition according to the invention preferably ranges from 7 to 12, more preferably from 8 to 11, most preferred from 9 to 11.

20

The pH of the cleaning composition of the invention may be adjusted with organic or inorganic acids or bases. Preferred inorganic bases are preferably alkali or alkaline earth hydroxides, ammonia, or bicarbonates, the alkali metal preferably being sodium or potassium or the alkaline earth metal preferably being calcium or magnesium. The organic bases are preferably amines, alkanolamines and other suitable amino compounds. Inorganic acids may include hydrochloric acid, sulphuric acid or phosphoric acid, and organic acids may include acetic acid, citric acid or formic acid as well as dicarboxylic acid mixtures such as Radimix (trade mark, Radici Group) and Sokalan DCS (trade mark, BASF).

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Other optional ingredients

The compositions may contain other ingredients which aid in their cleaning performance. For example, they may contain detergent builders and mixtures of builders in an amount of up to 25%, in particular when the composition contains one or

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- 15 -

more anionic surfactants. If present, the builder preferably will form at least 0.1% of the cleaning composition. Suitable inorganic and organic builders are well known to those skilled in the art.

5 A further optional ingredient for compositions used according to the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use. Examples thereof are fatty acids or their salts (soap), isoparaffins, silicone oils and combinations thereof. Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium and ammonium salts of fatty
10 acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from palm oil, coconut oil and ground nut oil. When employed, the amount of fatty acid or soap can form at least 0.005%, preferably 0.1% to 2% by weight of the composition.

15

Where a hydrocarbon solvent is present at a sufficiently high level this may itself provide some or all of the required antifoaming activity.

Compositions may also contain, in addition to the ingredients already mentioned,
20 various other optional ingredients such as colourants, whiteners, optical brighteners, soil suspending agents, detergent enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), solvents, co-solvents, gel-control agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), hydrotropes and perfumes.

25

Liquid Dispensers

The liquid composition of the invention may be stored in and dispensed by any suitable means, but spray applicators are particularly preferred. Pump dispensers (whether
30 spray or non-spray pumps) and pouring applicators (bottles etc.) are also possible. Thus, preferably the composition of the invention is comprised in a container, wherein the container comprises a spray dispenser for dispensing the composition in the form of a spray. The spray dispenser is preferably a trigger spray but may be any mechanical means for ejecting the liquid in spray or aerosol form.

35

Method for cleaning

In a second aspect the present invention provides A method for cleaning of a hard surface, wherein a composition according to the first aspect of the invention is used.

- 5 The method of the invention can be employed by the person skilled in the art. The result of the method is that a hard surface is easily cleaned without damage to the surface, as facilitated by the composition of the invention. Preferably, the composition is sprayed onto the surface using a spray dispenser.

10

DESCRIPTION OF FIGURES

Figure 1: Top: Scanning electron microscopy image (ruler width is 10 micrometer) and typical size indication of Whiscal® calcium carbonate rods (see Table 1);

1: X=0.974 micrometer; 2: Y=1 5.685 micrometer; 3: X=0.524 micrometer; 4:

15 Y=9.69 micrometer.

Bottom: Scanning electron microscopy image (ruler width is 2 micrometer) of Whiscal® calcium carbonate rods, indicated in circles a polygonal shape of the cross-section.

Figure 2: Scanning electron microscopy image (ruler width is 1 micrometer) of ViCALity ALBAFIL® (see Table 1); with determination of typical size of crystals.

20 1: X=0.33 micrometer; 2: Y=0.34 micrometer; 3: X=0.523 micrometer; 4: Y=0.479 micrometer.

Figure 3: Scanning electron microscopy image (ruler width is 10 micrometer) of Socal S2E (see Table 1); with determination of typical size of crystals.

1: X=5.016 micrometer; 2: Y=6.524 micrometer; 3: X=3.587 micrometer; 4:

25 Y=3.706 micrometer;

Figure 4: Scanning electron microscopy pictures of various types of acicular calcium carbonate crystals (see Table 4 in example 2).

Figure 5: Rheology measurements (dynamic viscosity [Pa.s] as function of shear rate [s^{-1}]), compositions in Table 8, example 3. Legend to the curves:

- | | |
|--------------------------------------------------|--------------------------------------------------|
| 1: CaCO ₃ rods 20%, water, pH 7 | 4: CaCO ₃ rods 20%, water, SMFP, pH 7 |
| 2: CaCO ₃ rods 20%, water, pH 10 | 5: CaCO ₃ rods 20%, water, TSP, pH 7 |
| 3: CaCO ₃ rods 20%, water, SMFP, pH 7 | 6: CaCO ₃ rods 20%, water, TSP, pH 10 |

Figure 6: Rheology measurements (dynamic viscosity [Pa.s] as function of shear rate [s^{-1}]), compositions in Table 9, example 3. Legend to the curves:

- | | |
|-----------------------------------------|-----------------------------------------|
| 1: $CaCO_3$ rods 30%, water, pH 7 | 4: $CaCO_3$ rods 30%, water, SMFP, pH 7 |
| 2: $CaCO_3$ rods 30%, water, pH 10 | 5: $CaCO_3$ rods 30%, water, TSP, pH 7 |
| 3: $CaCO_3$ rods 30%, water, SMFP, pH 7 | 6: $CaCO_3$ rods 30%, water, TSP, pH 10 |

Figure 7: Photographs of perspex surface, from example 4.

Left: before rubbing with cleaning composition

5 Middle: after rubbing with conventional composition with chalk

Right: after rubbing with composition with calcium carbonate rods according to the invention.

EXAMPLES

10 The following non-limiting examples illustrate the present invention.

Methods

Cleaning test

- 23 g of liquid abrasive cleaner (as described in Table 2) is placed on a pre-soiled
15 ceramic tile of known weight. The soil is prepared from calcium stearate, carbon black, and propan-2-ol (in a weight ratio of about 0.17:0.003:1), applied to the tile and baked in an oven at 180°C for 35 minutes.
- A 'WIRA' (is the Wool Institute Research Association scrubbing machine that moves a cloth in a motion that describes lissajous figures, in a regular, but non-
20 linear motion) is used to clean in a regular pattern for a set number of lissajous (1, 3 or 5 lissajous in this analysis, with 1 lissajous = 16 cycles), with a 992 g head weight.
- The liquid abrasive cleaner is then washed off the tile, which is then allowed to dry.
- The tile is re-weighed and the percentage soil removal calculated.
- 25 • 3 replicates for each product.

Damage test

5 g of liquid abrasive cleaner (as described in Table 2) is placed on a damp cloth ('Ballerina', ex Unilever) (2.5 cm × 12 cm) and mounted on a linear scrubbing device
30 (Erichsen).

The cloth is moved in a linear motion 80 times over a clean perspex surface (perspex = polymethyl methacrylate - PMMA).

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Three different head weights ('low', 'medium', 'high') are used in this analysis, respectively, to assess the different levels of damage cause by increased pressure.

'Low': no addition weight is added to the scrubbing head. 'Medium' 836 g weight added to scrubbing head. 'Heavy': a second weight is added to the scrubbing head giving a
 5 total additional weight of 1,327 g. The maximum pressure to be used is 80 g.cm^{-2} , The following pressure ranges are employed, respectively for the heads: $5\text{-}20 \text{ g.cm}^{-2}$, $15\text{-}50 \text{ g.cm}^{-2}$, and $25\text{-}80 \text{ g.cm}^{-2}$.

The perspex is measured over 7 points with a gloss meter before and after scrubbing to assess the loss of gloss to the surface. These measurements are carried out at 20°
 10 and 60° (reflectance angles at which the gloss is measured) and presented as a percentage loss of gloss. An angle of 20° is most relevant for a shiny surface.

Abrasive test

The pre-screening of raw materials for abrasion is done with an abrasion testing
 15 machine (Abrasion Tester AT2010, Leaderpower, China), and the number of revolutions is set at 87,000.

Pre-treatment of screen: Prepare 250 ml 0.5 wt% Alconox solution (Concentrated, anionic detergent, ex Alconox (White Plains, NY, USA), in sonic bath for 1 minute. Then put copper screen in the solution and sonicate for 5 minutes. Rinse the screen
 20 under hot running tap water for 3 minutes, holding with tweezer. Put the screen in distilled water and sonicate for 5 minutes, and 3 minutes more in distilled water. Heat

the screen at 105°C for 20 minutes and cool down in a desiccator. Weigh the screen on

a balance with at least 4 significant figures and record the data as W_{before} .

The copper screen is put at the bottom of fully dispersed raw material slurry (10.0 g of
 25 material in 90.0 g of water) and rubbed with PVC tube. After the testing, rinse the screen under hot running water until visible debris is removed. Then wash it with distilled water in sonic bath for 2 minutes, and 2 more minutes with running distilled water. At last, heat it at 105°C for 20 minutes and cool down in a desiccator. Re-weigh the screen and record the data as W_{after} .

30

The abrasion value is calculated by.

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$$abrasion \text{ [mg loss / 100,000 revolutions]} = \frac{100,000}{87,000} \times (W_{before} - W_{after})$$

Materials

5 Table 1 Properties and suppliers of calcium carbonate materials

<p>Calcium carbonate rods</p> <p>Whiscal (whisker-shaped calcium carbonate), precipitated calcium carbonate ex Maruo Calcium Company Ltd. (Akasi, Hyogo, Japan), consisting of aragonite rods/needles: average length 20 to 30 micrometer and average width 0.5 to 1.0 micrometer (see microscopy image in Figure 1)</p> <p>Specific gravity: 2.8; Bulk density: 0.07 g/cm³; Mohs hardness 3.5-4; pH 8.3-10.3 (10% cone. water solution)</p>
<p>ViCALity ALBAFIL® PCC</p> <p>ex Speciality Minerals Inc. (Bethlehem, PA, USA), a precipitated calcium carbonate, low lead content, calcite prismatic crystal structure, median particle size 0.7 micrometer, mode particle size 0.7 micrometer, bulk density: 0.29 g/cm³, tapped density: 0.60 g/cm³; specific density 2.71, pH 9.8; hardness: 3</p>
<p>Socal® S2E Food Grade</p> <p>ex Solvay Chemicals (Brussels, Belgium), a precipitated calcium carbonate, calcite scalenohedral crystal structure; Mean particle diameter (by air permeability) : 0.28 micrometer; particle size distribution d50: 2.2 micrometer; particle size distribution: 80 wt% < 3 micrometer (equivalent spherical diameter), 60 wt% < 2.3 micrometer, 40 wt% < 2 micrometer, 20 wt% < 1.2 micrometer. Mohs hardness: 3; Specific density: 2.71; free flowing density 200-400 g/L.</p>
<p>Omyacarb 30-AV</p> <p>ex Omya SpA (Milano, Italy), ground calcium carbonate powder, from white marble rock (Avenza-Carrara, Italy), CaCO₃ content 97.5%, calcite crystal mean particle size d50%: 35 micrometer (3% is larger than 100 micrometer; top cut d98%: 150 micrometer, 2% of particles is smaller than 2 micrometer); density : 2.6 - 2.8 g/cm³ (20 °C); bulk density: 1.6 g/cm³; pH : 8.5 - 9.5 (100 g/L, 20 °C)</p>

Omyacarb 65-AV
 ex Omya SpA (Milano, Italy), ground calcium carbonate powder, from white marble rock (Avenza-Carrara, Italy), CaCO_3 content 97.5%, calcite crystal
 mean particle size d50%: 54 micrometer (<0.1% is larger than 300 micrometer; top cut d98%: 250 micrometer); density : 2.6 - 2.8 g/cm³ (20 °C); bulk density: 1.6 g/cm³; pH : 8.5 - 9.5 (100 g/L, 20 °C)

Table 2 Standard composition of liquid abrasive cleaner

<i>Ingredient</i>	<i>Tradename</i>	<i>Supplier</i>	<i>concentration [wt%]</i>
PREMIX			
Demineralised water 50°C		In house	12.775
LAS Acid (linear alkylbenzene sulfonic acid)			4.91
Caustic soda			0.70
Tallow-based oleic acid	Priolene 6907	Croda	0.348
Hydrophobically modified Alkali Soluble acrylic polymer Emulsion	Acusol 820	Rohm Haas	0.030
MAIN MIX			
Demineralised water 50°C			to 100%
Silicone antifoam	Silicone DB-310	Dow Corning	0.006
Preservative (1,2-benzisothiazolin-3-one)	Proxel GXL	Zeneca	0.016
Sodium carbonate			3.0
<i>Calcium carbonate abrasive</i> (various combinations tested, see Table 3)			20.0
Titanium dioxide		Kemira	0.007
Surfactant	Lialet 125-5	Sasol	1.875
Perfume		Firmenich	0.330
Butyl digol		Dow	1.0
Premix		<i>made in house</i>	19.675

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First the premix is made, involving reacting LAS Acid with caustic soda to produce anionic surfactant. The premix is mixed with the other ingredients of the main mix.

Example 1: Testing acicular calcium carbonate

- 5 The following compositions of liquid abrasive cleaners containing various forms of calcium carbonate abrasive were tested in the formulations as disclosed in Table 2. The cleaning and damage results are given in the following table. Some samples on 1, 3, or 5 lissajous tested

Table 3 Combinations of calcium carbonate abrasives used in the composition of Table 2, results on cleaning (1, 3, or 5 lissajous), damage (using 3 weights), and ratio between cleaning and damage.

<i>Formulation</i>	<i>Cleaning test:</i> Soil removal after x lissajous [%]			<i>Damage test:</i> Loss of Gloss at 20° using x weight: [%]			<i>Ratio Cleaning 5 lissajous : Damage heavy weight [unit]</i>
	5	3	1	<i>Heavy</i>	<i>Medium</i>	<i>Low</i>	
Omyacarb 30-AV 10% and Omya- carb 65-AV 10% (comparative)	94.4 ± 5	-	-	25.7	19.8	10.3	3.7
Socal S2E 20% (comparative)	98.9 ± 5	-	-	13.9	-	-	7.1
Albafil 20% (comparative)	92.0 ± 5	-	-	10.0	6.3	0.8	9.2
Whiscal 5% and Omyacarb 30-AV 15%	93.0 ± 5	-	-	24.6	22.7	4.6	3.8
Whiscal 10% and Omyacarb 30-AV 10%	87.8 ± 5	-	-	13.9	15.4	3.6	6.3
Whiscal 15% and Omyacarb 30-AV 5%	89.0 ± 5	-	-	6.6	3.8	-1.1	13.5
Whiscal 20%	75.4 ± 5	-	-	0.3	0.6	0.5	251.3
Whiscal 10% and Albafil 10%	88.6	58.5	19.9	2.3	-	-	38.4
Whiscal 5% and Albafil 15%	92.3	60.2	19.4	5.3	3.6	1.3	17.4

- 5 The (fictive) ratio between cleaning and damage is a measure for the relation between cleaning and damage: a high value of this number gives a good cleaning result and little damage, while a low value indicates that either the cleaning performance decreases or the damage increases high, or both.

These results show that using the acicular rods according to the invention show less damage than the standard calcium carbonate of the prior art. The more acicular calcium carbonate is used, the less the damage to the surface to be cleaned. Also S2E and Albafil lead to less damage to the surface to be cleaned, compared to the formulations with Omyacarb 30-AV and 65-AV. If the concentration of Omyacarb 30-AV and 65-AV is at least 10% by weight, then the damage is relatively high. The combination of Whiscal and Albafil also leads to a product with good abrasive strength, and only little damage.

Example 2: Testing various types acicular calcium carbonate rods

Various rod-type calcium carbonate crystals were tested in this example. Both commercially available calcium carbonate, as well as samples prepared on laboratory scale were tested.

Table 4 Sources of various types acicular calcium carbonate rods, all precipitated calcium carbonate.

<i>Material</i>	<i>Supplier</i>	<i>Trade Name</i>	<i>Notes</i>
CaCOs rods 1	Maruo Calcium Co. Ltd.	Whiscal (from Table 1)	Industrial grade, commercially available
CaCOs rods 2	Qinghai Institute of Salt Lakes, Chinese Academy of Sciences (Xining, Qinghai, China)		Experimental sample
CaCOs rods 3	<i>Same as rods 2</i>		Experimental sample
CaCOs rods 4	<i>Same as rods 2</i>		Experimental sample
CaCOs rods 5	Maruo Calcium Co. Ltd.		Lab scale (prepared similarly as Rods 1)
CaCOs rods 6	<i>Same as rods 2</i>		Commercially available

Table 5 Properties of various types acicular calcium carbonate rods

Material	Length [micro-meter]	Width [micrometer]	Aspect Ratio	Abrasion value [mg/100,000r]
CaCO ₃ rods 1 (Whiscal from Table 1)	20-30	0.5-1.0	20-60	7.82
CaCO ₃ rods 2	10-50	1-3	20-30	17.4
CaCO ₃ rods 3	5-30	0.5-2	10-15	22.0
CaCO ₃ rods 4	5-40	1-2	5-20	26.7
CaCO ₃ rods 5	0.3-1.0	0.1-0.3	2-8	4.8
CaCO ₃ rods 6	50-80	3-5	20-30	41.4

Properties of rods 1 were obtained from the supplier. The properties of rods 2 to 7 were determined by counting 50 rods from a scanning electron microscopy image.

5

Each of these rods were tested in the liquid abrasive cleaner of Table 2, on cleaning and damage. The rheological properties of these formulations are given in the following table. The rheological properties were determined using the following protocol:

- Instrument - Paar Physica - MCR300 with Automatic Sample Changer (ASC)
- Geometry - CC27, profiled DIN concentric cylinder
- Temperature - 25°C
- Protocol - Three step method:

Step 1 - Controlled stress steps from 0.01 to 400 Pa; 40 steps logarithmically spaced in stress with 40 s being spent at each point to measure the shear rate (and hence viscosity); Step 1 is terminated once a shear rate of 0.1 s⁻¹ is reached.

Step 2 - Controlled shear rate steps from 0.1 to 1200 s⁻¹; 40 steps logarithmically spaced in shear rate with 6 seconds being spent at each point to determine the stress required to maintain the shear rate and hence the viscosity.

Step 3 - Controlled shear rate steps from 1200 to 0.1 s⁻¹; 40 steps logarithmically spaced in shear rate with 6 seconds being spent at each point to determine the stress required to maintain the shear rate and hence the viscosity.

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The results of the first two steps are combined being careful to remove any overlap and to ensure that the required shear rates were achieved at the start of the step.

The rheology is described in terms of the pouring viscosity (in Pa.s) at a shear rate of 21 s^{-1} and the yield stress of the system in Pa. The yield stress is taken to be the value of the stress at a shear rate of 0.1 s^{-1} . The yield stress indicates at which stress the material starts to deform plastically (the yield point), i.e. it flows as a liquid. At lower stress values than the yield stress (prior to the yield point) the material will deform elastically and will return to its original shape when the applied stress is removed. Once the yield point is passed, some fraction of the deformation will be permanent and non-reversible.

The composition in Table 2 was prepared for each calcium carbonate rods in Table 4, as well for the reference.

15

Table 6 Rheological properties of compositions from Table 2 containing various types acicular calcium carbonate rods

<i>Formulation</i>	<i>Yield Stress [Pa]</i>	<i>Pouring viscosity [Pa s]</i>
Omyacarb 30-AV 10% and Omyacarb 65-AV 10% (<i>comparative</i>)	10.1	0.532
CaCO ₃ rods 1 (Whiscal from Table 1) 20%	12.6	0.705
CaCO ₃ rods 2 20%	5.4	0.441
CaCO ₃ rods 3 20%	6.0	0.455
CaCO ₃ rods 4 20%	9.1	0.595
CaCO ₃ rods 5 20%	8.1	0.582
CaCO ₃ rods 6 20%	5.8	0.470

The highest yield stress is obtained for the product containing the Whiscal rods. This product also has the highest viscosity when pouring. The product with the highest yield stress has the best ability to suspend a dispersed phase (i.e. denser or bigger particles). These pouring viscosities determine how easy it is to pour or squeeze the product from a packaging material. Practically the ease of squeeze is dominated by the stiffness of the packaging.

25

Table 7 Results of cleaning (1, 3, or 5 lissajous), damage (using 3 weights), and ratio between cleaning and damage of compositions from Table 2 containing various types acicular calcium carbonate rods

Material	Cleaning test: Soil removal after x lissajous [%]			Damage test: Loss of Gloss at 20° using heavy weight [%]	Ratio Cleaning at x lissajous : Damage [unit]		
	5	3	1		5	3	1
Omyacarb 30- AV 10% and Omyacarb 65- AV 10% (comparative)	94.4			25.7	3.7		
CaCO ₃ rods 1 (Whiscal from Table 1) 20%	75.4	60.3	27.4	0.3	251.3	201.0	91.3
CaCO ₃ rods 2 20%	84.3	60.6	24.0	9.1	9.3	6.7	2.6
CaCO ₃ rods 3 20%	82.0	62.0	25.7	18.7	4.4	3.3	1.4
CaCO ₃ rods 4 20%	91.9	56.6	24.9	23.1	4.0	2.5	1.1
CaCO ₃ rods 5 20%	90.9	57.6	n.a.	3.3	27.5	17.5	
CaCO ₃ rods 6 20%	82.3	55.9	28.2	18.2	4.5	3.1	1.5
CaCO ₃ rods 7 20%	86.7	61.4	n.a.	9.2	9.4	6.7	

- 5 The (fictive) ratio between cleaning and damage is a measure for the relation between cleaning and damage: a high value of this number gives a good cleaning result and little damage, while a low value indicates that either the cleaning performance decreases or the damage increases high, or both.
- 10 Here the reference sample (prior art composition with Omyacarb) has a value of 3.7. Any value higher than this can be considered to be a good result, while a lower value

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does not have a good result. Please note that the results should be compared between the same number of lissajous. In this case all rods have a higher value than the comparative example. Especially the rods 1 and 5 show good results. These rods have a width generally less than 1 micrometer.

5

Example 3: Liquid abrasive cleaner with phosphate or fluorophosphate ions

The effect of phosphate ions on the rheology of a composition containing calcium carbonate rods was investigated.

10 *Materials*

- Trisodium phosphate dodecahydrate (TSP, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), supplier: Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China);
- Sodium monofluorophosphate (SMFP, $\text{Na}_2\text{PO}_3\text{F}$), supplier: Research Institute of Physical and Chemical Engineering of Nuclear Industry, Huahe New-Technology Development Company (Tianjin, China);
- Calcium carbonate rods: Whiscal ex Maruo (see example 1, Table 1).

15

Rheology measurements

CaCO_3 rods are mixed with 60g water while stirring. Optionally additives SMFP or Na_3PO_4 were added into the mixture while stirring. Optionally after 15 minutes concentrated NaOH solution (10 mol/L) was added into the mixture drop by drop until the pH reaches about 10. The mixture is stirred for 10 minutes. At last the sample is ready for rheology test.

20

25 Rheology was determined using a rheometer Physica MCR 301 (Anton Paar, Austria), at variable shear rate ($0.001\text{-}1000\text{ s}^{-1}$), geometry: PP50/TG SN6884, profile: ram log.

The following formulations were prepared to determine rheology (Table 8).

Table 8 Compositions of formulations for rheology measurements, rheology data in Figure 5.

Sample#	CaCO ₃ rods 1 (Whiscal) [g]	Water [g]	SMFP [g]	TSP [g]	pH (adjusted by NaOH)
1	20	60	-	-	7 (no NaOH)
2	20	60	-	-	10 (NaOH)
3	20	60	1.1	-	7 (no NaOH)
4	20	60	1.1	-	10 (NaOH)
5	20	60	-	2.55	7 (no NaOH)
6	20	60	-	2.55	10 (NaOH)

The corresponding rheology data are given in Figure 5.

5

Table 9 Compositions of formulations for rheology measurements, rheology data in Figure 6.

Sample#	CaCO ₃ rods 1 (Whiscal) [g]	Water [g]	SMFP [g]	TSP [g]	pH (adjusted by NaOH)
1	30	60	-	-	7 (no NaOH)
2	30	60	-	-	10 (NaOH)
3	30	60	1.1	-	7 (no NaOH)
4	30	60	1.1	-	10 (NaOH)
5	30	60	-	2.55	7 (no NaOH)
6	30	60	-	2.55	10 (NaOH)

The corresponding rheology data are given in Figure 6.

10

The data show that the addition of phosphate ions or fluorophosphate ions leads to a lower viscosity of the formulation containing calcium carbonate rods, especially at a shear rate smaller than about 10 s⁻¹. The effect is shown both at pH 7 and pH 10.

15 Therewith a composition can be made, that has a relatively high content of calcium carbonate for abrasive cleaning, that does not strongly damage the hard surface, and

that has a relatively low viscosity, as compared to a composition without the phosphate ions.

Example 4: Polishing effect of the particulate calcium carbonate abrasive

- 5 Two formulation prototype of liquid abrasive cleaners were prepared. One is a typical formulation like in table 2, containing 45% of calcite chalk 30-AV (see table 1), abbreviated as 'Chalk'. The other formulation contained 30% CaCO_3 rods 1 (Whiscal, see table 1), abbreviated as 'Rods'.
- 10 For polishing black perspex (made of PMMA) was used as substrate. The perspex template was separated into test regions of 5x10 cm. Firstly, the gloss value of perspex before start was measured and recorded by Glossmeter (Multi Gloss 268plus, Konica Minolta) as **G₀**.
- Then 2.5 g 'Chalk' formulation was applied onto the test region. The sample was
- 15 rubbed with damp cloth ('Ballerina', ex Unilever) in X direction under a normal force (vertical) of around 1.5 kg (by hand, recorded by Ergo-rig) for 60 seconds. After that, the test region was cleaned by tap demineralised water for 1 minute. Then gloss value was measured and recorded as **G_d**. Subsequently, 2.5g of 'Rods' formulation was added onto test region and rubbed in Y direction at the same loading force for
- 20 60 seconds. The substrate was cleaned again and gloss value was recorded as **G_p**. All data points were measured from the middle of the test region.

To define a polishing benefit, surface recovery ratio is applied as following:

25 $\text{Recovery\%} = (\text{G}_p - \text{G}_d) / (\text{G}_0 - \text{G}_d) \times 100\%$

The result of the gloss values and the recovery are the following:

	•	<i>G₀</i>	79.7
	•	<i>G_d</i>	42.4
30	•	<i>G_p</i>	73.2
	•	Recovery%	82.6%

These data show that the perspex surface is damaged after rubbing with a conventional cleaner with chalk, and then the surface is polished again with the liquid

35 with rods. The recovery of the surface is about 82% of its initial value. Figure 7 shows

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photographs of the surface of the perspex before and after rubbing with the compositions. These pictures indeed show that the before rubbing the surface of the perspex is smooth and shiny (left). After rubbing with the conventional composition, many scratches are visible, the surface seems to have become more grey than black (middle picture). After the rubbing with the composition with the rods, the perspex surface has become smooth and black again (right picture), clearly a polishing effect.

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CLAIMS

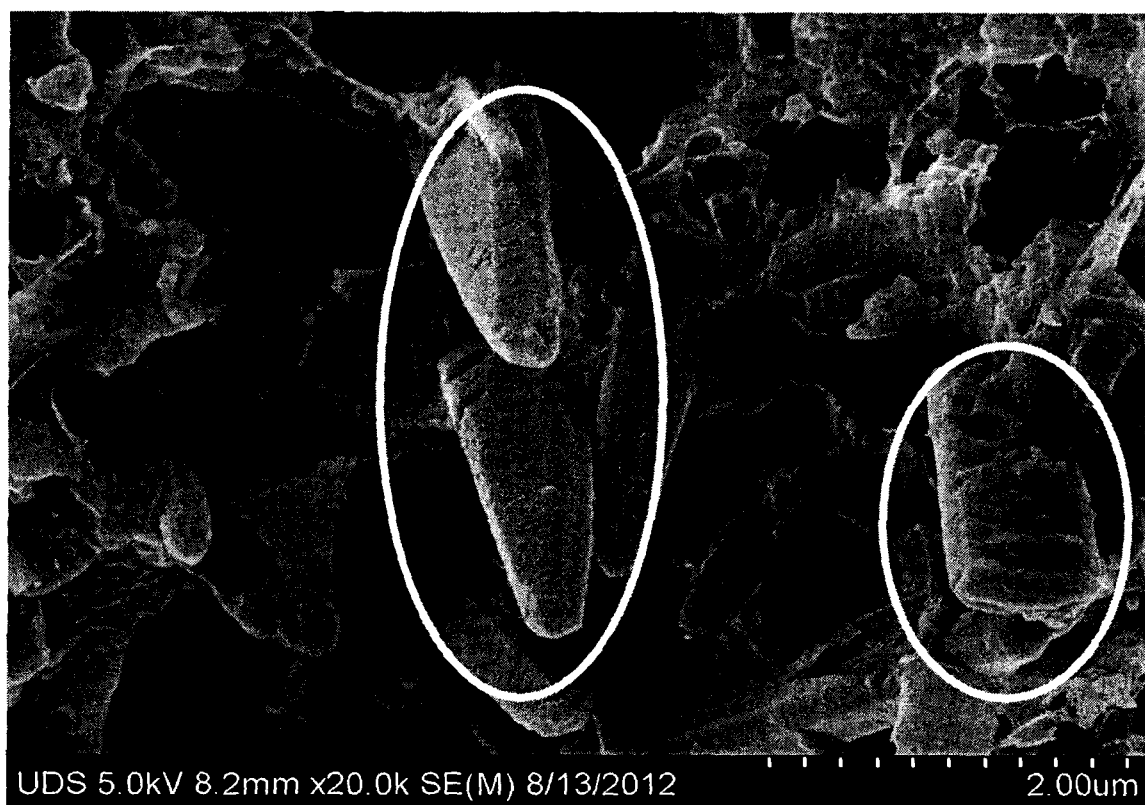
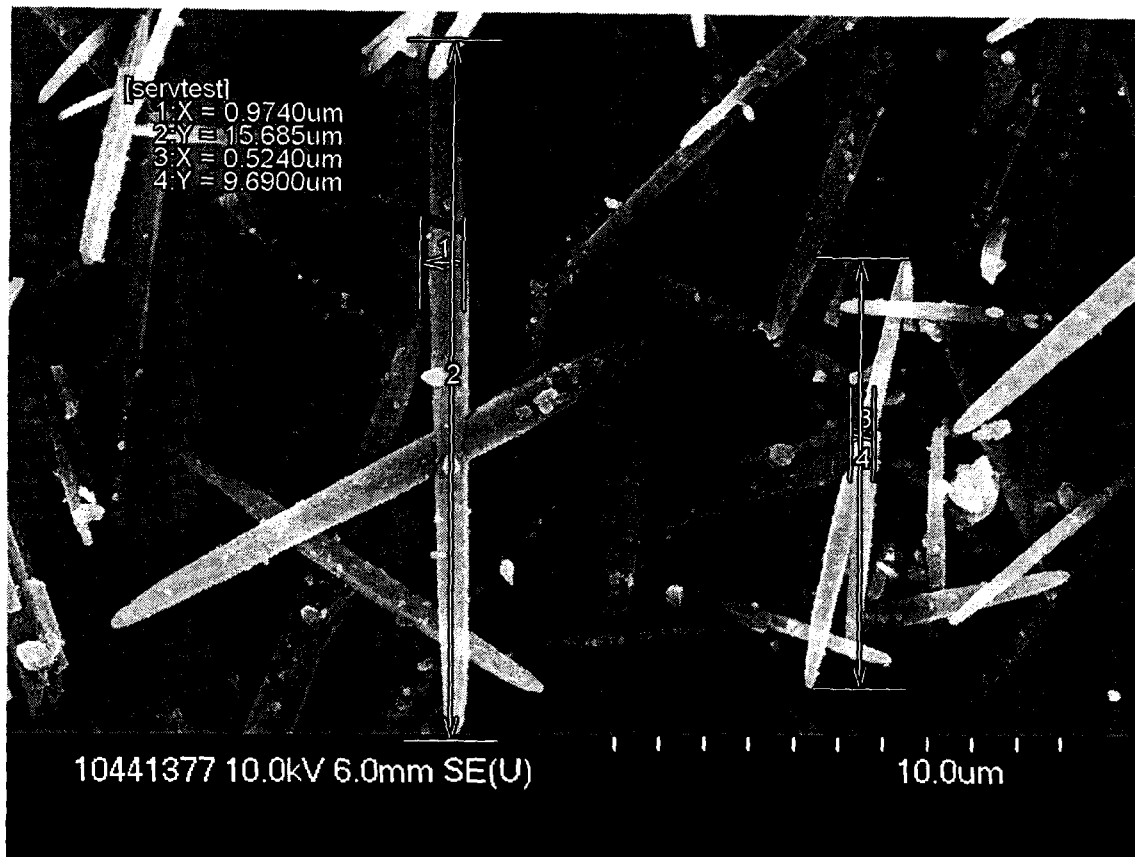
1. A liquid composition for cleaning of hard surfaces, comprising surfactant, and a particulate calcium carbonate abrasive composed of primary particles which are acicular and which have a length of 2 micrometer or more, in which the level of the particulates ranges from 2 to 40% based on the total weight of the composition.
2. A composition according to claim 1, wherein the calcium carbonate abrasive comprises a crystalline calcium carbonate in which the crystals are acicular with a largest dimension of 2 micrometer or more.
3. A composition according to claim 1 or 2, in which the crystals are acicular aragonite with a length ranging from 2 to 100 micrometer, preferably from 10 to 50 micrometer.
4. A composition according to any of claims 1 to 3, wherein the crystals are acicular aragonite with a width ranging from 0.1 to 4.0 micrometer, preferably from 0.1 to 1.0 micrometer.
5. A composition according to any of claims 1 to 4, wherein the crystals are acicular aragonite with an aspect ratio ranging from 2.5 to 1000, preferably from 10 to 100.
6. A composition according to any of claims 1 to 5, wherein the crystals have a cross-sectional shape which is polygonal.
7. A composition according to any of claims 1 to 6, wherein the concentration of calcium carbonate abrasive ranges from 5 to 30%, preferably from 10 to 25%, based on the total weight of the composition.
8. A composition according to any of claims 1 to 7, wherein the composition further comprises phosphate ions and/or halophosphate ions, preferably phosphate ions and/or fluorophosphate ions.

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9. A composition according to claim 8, wherein the weight ratio between calcium carbonate abrasive and phosphate ions and/or halophosphate ions ranges from 200:1 to 10:1, preferably from 80:1 to 20:1.
10. A composition according to any of claims 1 to 9, further comprising ground calcium carbonate in the form of calcite crystals.
11. A composition according to claim 10, wherein the amount of particulate calcium carbonate abrasive composed of primary particles which are acicular is at least 50 wt% of the total amount of calcium carbonate, preferably at least 75 wt%.
12. A composition according to any of claims 1 to 11, wherein the composition further comprises particulate precipitated calcium carbonate with a calcite crystal structure, having a largest dimension ranging from 0.1 to 10 micrometer, preferably from 0.4 to 4 micrometer, and a ratio between largest and smallest dimension ranging from 1 to 10, preferably from 1 to 5.
13. A composition according to claim 12, wherein the particulate precipitated calcium carbonate with a calcite crystal structure has a prismatic crystal structure, with a largest dimension ranging from 0.1 to 2 micrometer, preferably from 0.2 to 1 micrometer.
14. A composition according to claim 12, wherein the particulate precipitated calcium carbonate with a calcite crystal structure has a scalenohedral crystal structure, and wherein the crystals are agglomerated, and wherein the agglomerate has a largest dimension ranging from 1 to 20 micrometer, preferably from 2 to 15 micrometer.
15. A method for cleaning of a hard surface, wherein a composition according to any of claims 1 to 14 is used.
16. A method for polishing of a hard surface, wherein a composition according to any of claims 1 to 14 is used.
17. A method according to claim 15 or 16, wherein the composition is sprayed onto the surface using a spray dispenser.

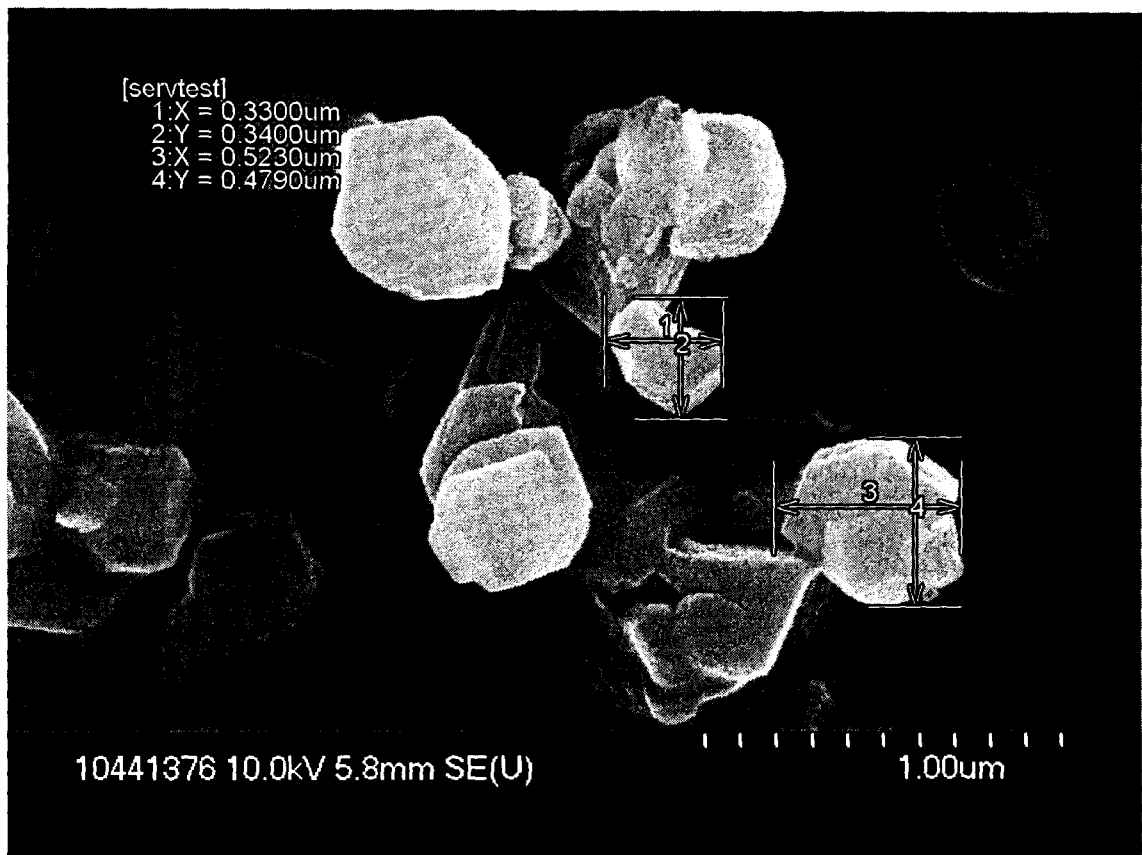
- 1/6

Figure 1/7



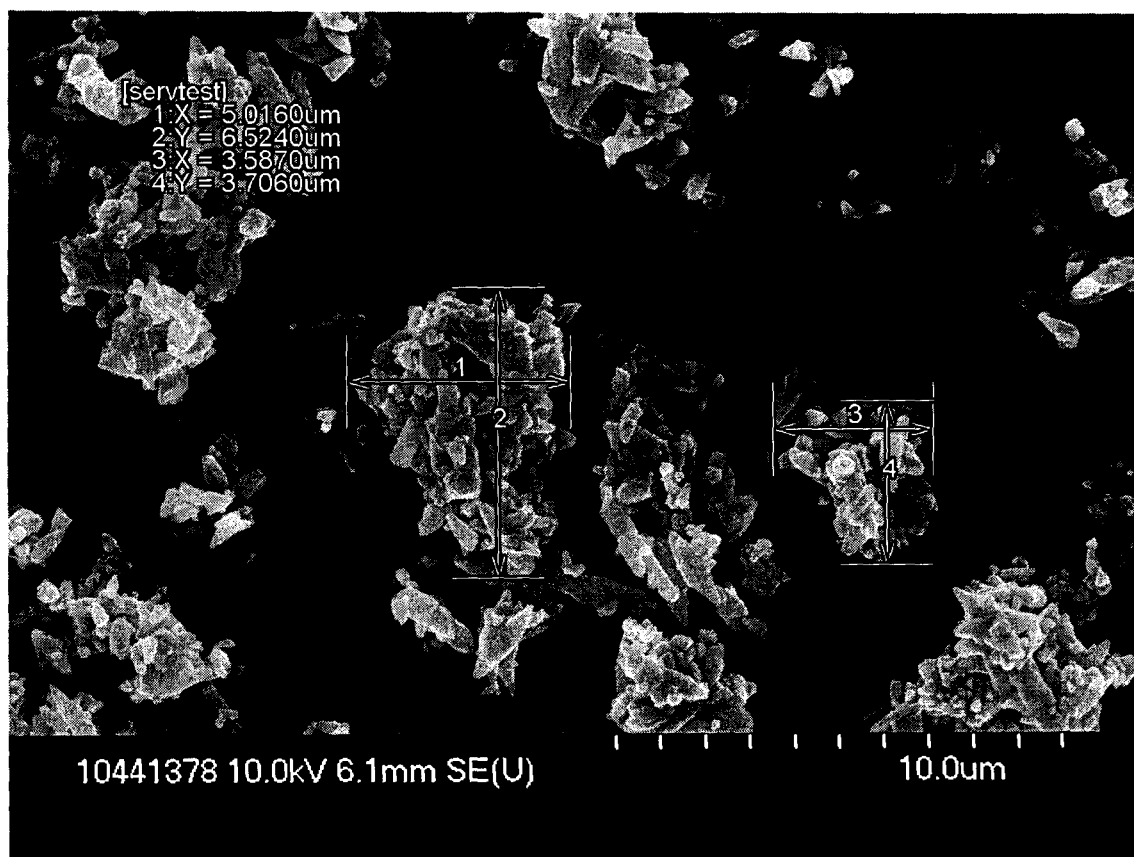
-2/6

Figure 2/7



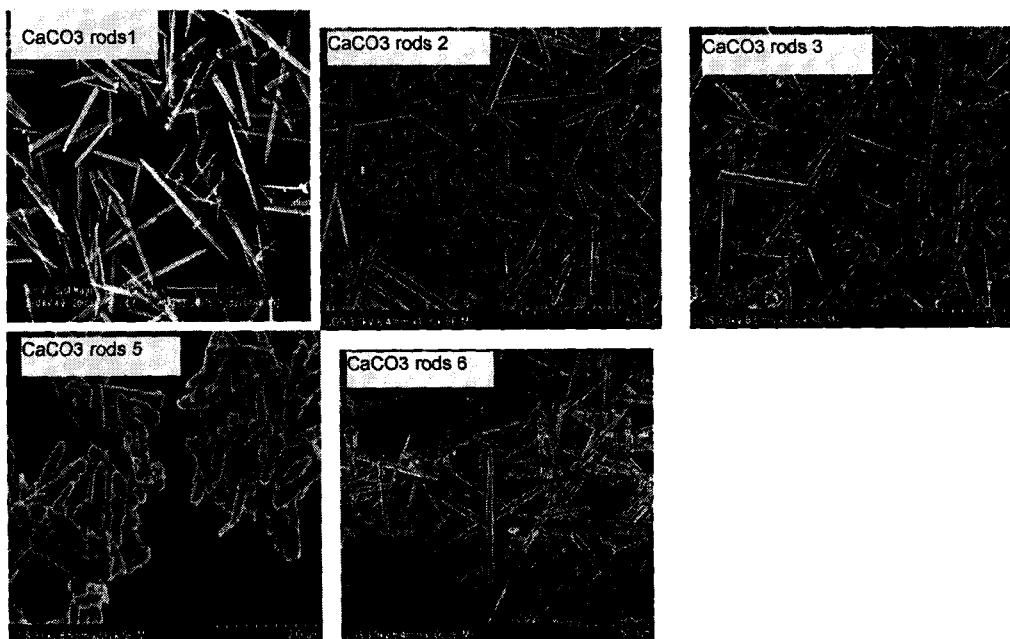
-3/b

Figure 3/7



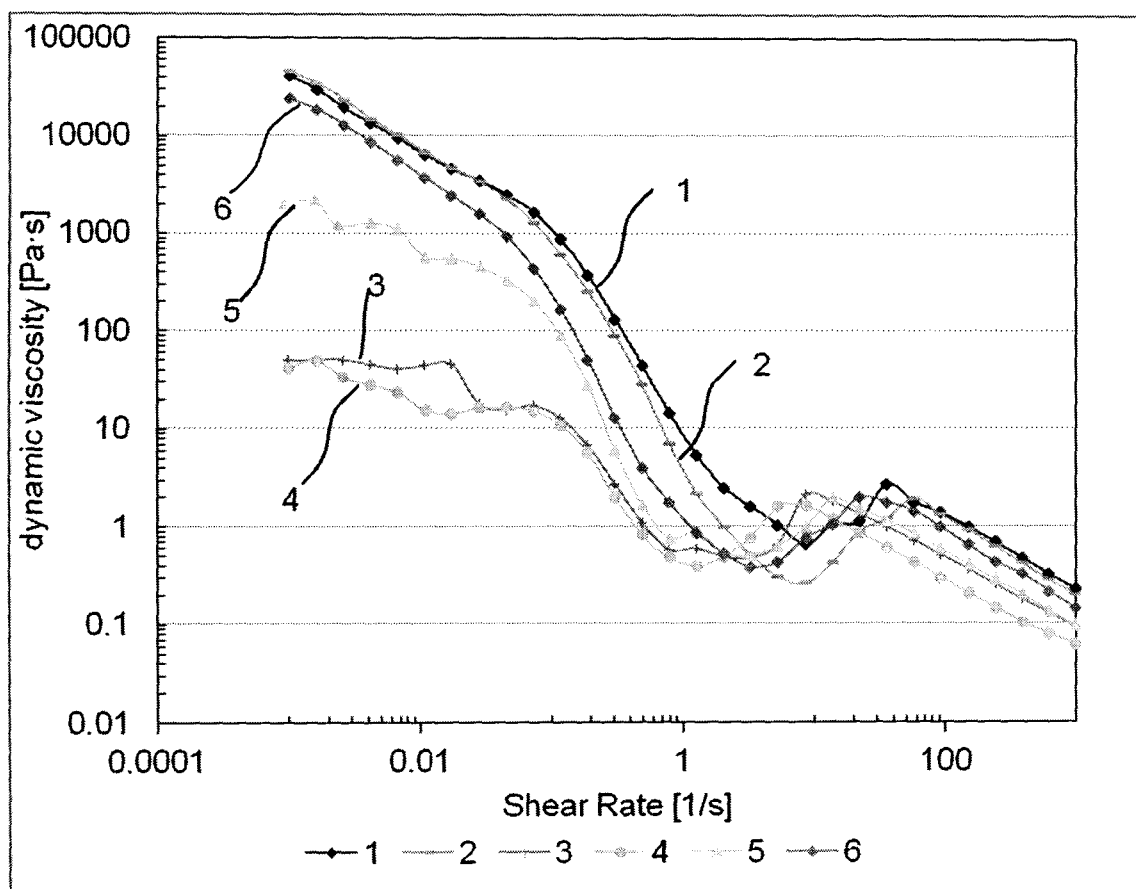
- 4 / 6

Figure 4/7



-5/6

Figure 5/7



$-6/6$

Figure 6/7

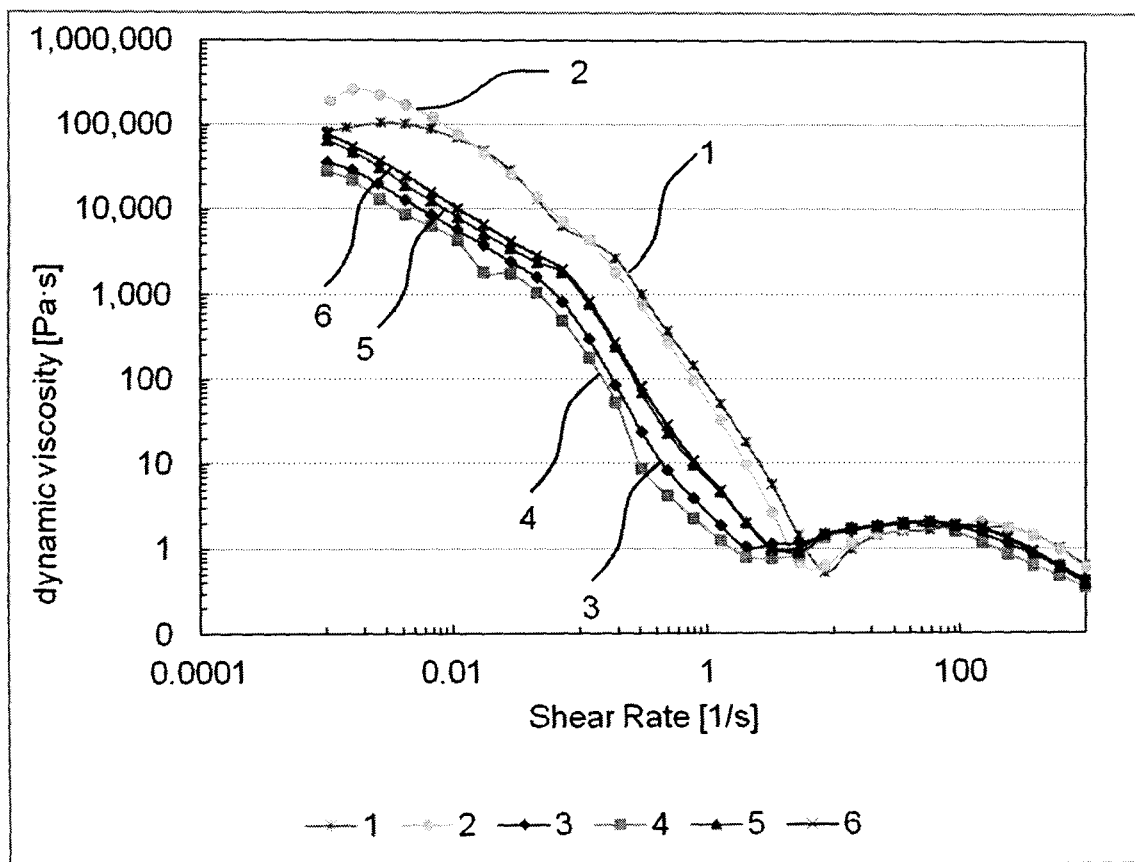
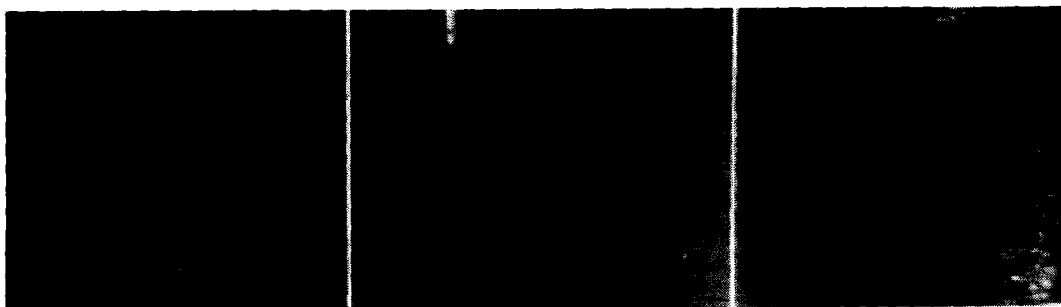


Figure 7/7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/084669

A. CLASSIFICATION OF SUBJECT MATTER

CUD 3/10(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C 11D/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,EPODOC,WPI, CALCIUM CARBONATE, CaCO₃, ACICULAR, ARAGONITE, TIP, TAPER, SHRILL,
NEEDLE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category ¹ *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP0103325A1 (UNILEVER NV. et al.) 21 Mar. 1984 (21.03.1984) Claim 1	1-17
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A	US5151208A (LEVER BROS. CO. DIVISION OF CONOPCO, INC.) 29 Sep.1992 (29.09.1992) Examples 1-6	1-17
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A	US5164172A (MARUO CALCIUM CO. LTD.) 17 Nov.1992 (17.11.1992) Examples 1-10	1-17

I Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search 10Jan.2013 (10.01.2013)	Date of mailing of the international search report 28 Feb. 2013 (28.02.2013)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer ZHANG, Wei Telephone No. (86-10)82245740

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Information on patent family members

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International application No.
PCT/CN2012/084669

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