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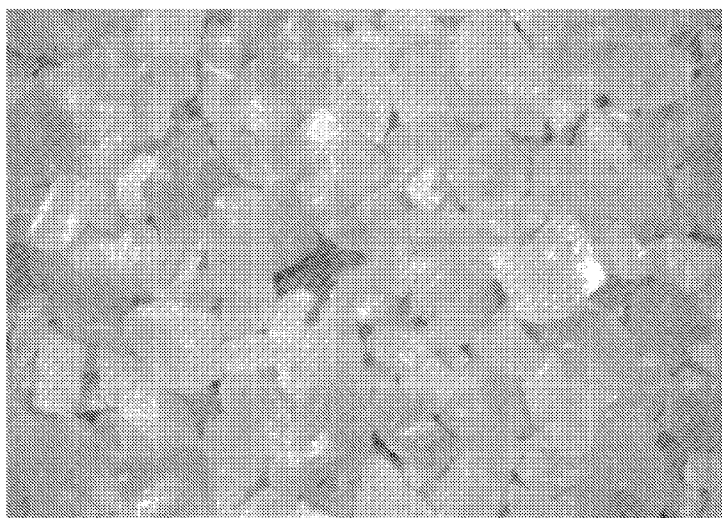
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(54) Title: ALKALINE EARTH CARBONATE CONTAINING MINERAL FOR SURFACE CLEANING

Figure 2



(57) Abstract: The present invention relates to a dry blasting process for the cleaning of solid surfaces as well as special abrasive pigments suitable therefor and a method for their production.



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Alkaline Earth Carbonate Containing Mineral for Surface Cleaning

The present invention relates to a dry blasting process for the cleaning of solid
15 surfaces as well as to special abrasive pigments suitable therefor and a method for
their production.

Blast cleaning, also called sand blasting or bead blasting is a generic term for the
process of smoothing, shaping and cleaning a hard surface by forcing solid particles
20 across that surface at high speeds using compressed air. The effect is similar to that
of using sandpaper, but provides a more even finish with no problems at corners or
crannies.

There is a continuous search for new materials and improved techniques of blast
25 cleaning due to numerous disadvantages of the materials previously used.

Historically, the material used for sandblasting was sand that had been sieved to a
uniform size. However the silica dust produced in the sandblasting process caused
silicosis after sustained inhalation of dust. Sandblasting may now only be performed
in a controlled environment using ventilation, protective clothing and breathing air
30 supply.

Other materials for sandblasting have been developed to be used instead of sand; for
example, steel grit, steel shots, copper slag, glass beads (bead blasting), metal pellets,
dry ice, corundum, and even ground coconut shells or corncobs.

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The blast cleaning technique is used for the cleaning of various materials such as metal containers, boat hulls, bricks and concrete work. It is used for cleaning industrial as well as commercial structures.

5

There are many different techniques of blast cleaning, such as e.g. dry blasting and wet blasting.

10 Wet blasting has many advantages over dry blasting such as no dusting and blasting without surface damage. Wet blasting is accomplished by injecting the abrasive into a pressurized water stream or creating a slurry of abrasive and water that is pressurized or introduced into a compressed air stream.

15 However, there are many applications which need dry conditions, e.g. due to water-sensitivity of the surfaces or blasting material, in which cases wet blasting cannot be used.

20 Thus, there is a continuous need for dry blasting materials and techniques providing the maximum safety for the operator by minimum dusting, but at the same time effective cleaning without damaging the surfaces.

In the prior art there were several suggestions for improved blast cleaning, most of which however relate to wet blast cleaning or insufficient abrasive materials as blasting agents.

25

For example, DE 42 22 884 A1 relates to a method of smooth cleaning building facades by dry blasting, wherein an abrasive blasting agent is entrained in a pressurised air jet. However, the blasting agent consists of a mixture of glass pearls of 70 to 110 microns grain size, normal corundum of 44 to 74 micron grain size, and 30 mixed corundum of 53 to 88 microns grain size, i.e. material not having dusting

problems, but being very hard and sharp-edged, respectively, thus having a detrimental effect on a number of surfaces to be cleaned.

In US 6,113,475 a method of cleaning a container is described and an apparatus
5 therefor for cleaning a surface layer of the container by blasting fine particles of sodium bicarbonate with pressurized air into the container. However, sodium bicarbonate is a very soft material which is only suitable for very special coatings. Thus, it is also mentioned in this document that the method is used for the exfoliation of paint or the like, a prerequisite for which is that the surface to be cleaned must be
10 very even in order to make exfoliation possible. Otherwise, the paints must be soft or unhardened. Furthermore, sodium bicarbonate is hygroscopic and soluble in water and therefore not suitable for the removal of aqueous or moist deposits from surfaces.

15 WO 94/07658 A1 relates to a blasting agent for removing coatings like paint, oxides, scales and the like from metals, alloys, composites and similar substrates, and a process for removing said coatings. The blasting agent comprises a precipitate or agglomerate of water-insoluble calcium carbonate, magnesium carbonate or mixtures thereof and 0-30 weight % alkali sulphate and/or magnesium sulphate. Preferably,
20 the blasting agent is precipitated calcium carbonate or agglomerates thereof having a particle size of 10-200 μm , preferably 40 to 80 μm . According to the teaching of this document precipitates and agglomerates are essential for avoiding damages to the treated surfaces as it was found that natural water-insoluble carbonate particles like dolomite have a structure which is predominantly crystalline leaving profiles or
25 grooves in the surface.

In US 5,827,114 a slurry blasting process is described employing a liquid carrier medium containing a dispersed water-soluble particulate abrasive to enhance blast
30 accelerator stream which may be aqueous or non-aqueous such as glycerine.

US 5,531,634 relates to a method for blast cleaning a solid surface using an abrasive composition of calcium carbonate, wherein a coarse, medium, or fine grade of calcium carbonate having an average Mohs hardness of 4.25, i.e. a very hard kind of calcium carbonate can be used. The blasting medium can be pressurized air, but for the control of dust water is injected into the nozzle. The use of the different grades depends on the surface to be cleaned, i.e. the softer the surface, the finer the grade. The coarse grade can only be used for hard surfaces in view of the use of relatively hard calcium carbonate.

10

In EP 1 467 841 A1 a further process for removing a coating from a surface is suggested. This process is described as an erasing process which has to comply with a number of requirements. The erasing agent which may be made up of calcium carbonate comprises a plurality of particles in the form of precipitates or agglomerates and the blasting has to be carried out in a specific angle of incidence of the particles and the surface of between 0° and 60° is required in order to let the round precipitates or agglomerates roll along the surface and thus absorb the coating. Otherwise, the process will not work.

15

Thus, the processes of the prior art still have several drawbacks. Either the blasting material is too hard and causes damage to the surface to be cleaned, or too soft leading to dusting or poor cleaning performance.

20

Also, the processes using alkaline earth carbonates can only be controlled by additional material, time and energy consuming steps, such as the use of liquids, or the provision of the calcium carbonate in the form of precipitates or agglomerates in order to provide effective cleaning without dusting or damaging the surface.

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- 5 -

Therefore, it is an object of the present invention to provide a process for the dry cleaning of solid surfaces causing little to no abrasion on the surface to be cleaned at a high cleaning efficiency and at low dust exposure.

- 5 Furthermore, it is an object of the present invention to provide mineral particles, which are suitable for the process according to the present invention, mineral particle of a natural source and as well as an easy method for the production of same.

10 The above object has been solved by a process for cleaning solid surfaces by dry blasting said surfaces with natural alkaline earth carbonate particles, having a median particle diameter of from 100 to 500 μm and a Mohs hardness of below 4, provided that the alkaline earth carbonate particles are not in the form of precipitates or agglomerates.

- 15 Natural alkaline earth carbonate which is especially suitable for the process of the invention is natural calcium carbonate and/or natural calcium magnesium carbonate and particularly natural alkaline earth carbonate being selected from the group comprising marble, chalk, dolomite, limestone and mixtures thereof.

- 20 Suitable natural alkaline earth carbonates for the present invention have an average Mohs hardness of preferably from 2.6 to 3.9, especially preferably from 2.6 to 3.4, e.g. 3.

25 The Mohs scale of hardness characterizes the scratch resistance of various minerals through the ability of a harder material to scratch a softer material. It was created in 1812 by the German mineralogist Friedrich Mohs and is one of several definitions of hardness in material science. Mohs based the scale on ten minerals that are all readily available. As the hardest known naturally occurring substance, diamond is at the top of the scale having a Mohs hardness of 10. The hardness of a material is measured
30 against the scale by finding the hardest material that the given material can scratch,

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and/or the softest material that can scratch the given material. For example, if some material is scratched by apatite (5) but not by fluorite (4), its hardness on the Mohs scale would fall between 4 and 5.

- 5 Particularly preferred is natural alkaline earth carbonate in the form of marble, especially dolomite containing marble, such as marble originating from South Tyrol (Italy), Kärnten (Austria) or Bergen (Norway).

Optionally, the natural alkaline earth carbonate can contain commonly used
10 additives, such as e.g. dry grinding aids and/or wetting agents.

The alkaline earth carbonate content in the natural alkaline earth carbonate mineral is preferably > 90 wt.-%, more preferably 95 to 99.9 wt.-%, e.g. 99.5 wt.-%.

- 15 The minerals suitable for the present invention furthermore can have a portion, which is insoluble in hydrochloric acid, in an amount of ≤ 10 wt.-%, preferably ≤ 5 wt.-%, more preferably ≤ 2.7 wt.-%, e.g. 0.5 wt.-%.

Preferred natural alkaline earth carbonate for the use in the present invention has a
20 calcium content of at least 21 wt.-%, preferably > 35 wt.-%, more preferably > 38 wt.-%.

Preferred natural alkaline earth carbonate for the use in the present invention has a
25 magnesium content of maximum 13 wt.-%, preferably < 3 wt.-%, more preferably < 1.5 wt.-%.

It is furthermore advantageous that the natural alkaline earth carbonate comprises dolomite in an amount of from 0.1 to 100 wt.-%, preferably from 2 to 10 wt.-%, more preferably from 3 to 7 wt.-%, e.g. 5 wt.-%.

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The alkaline earth carbonate used in the process of the present invention is essentially dry. "Essentially dry" in the sense of the present invention means a water content of below 5 wt.-%, preferably below 1 wt.-%, particularly below 0.1 wt.-% based on the weight of the alkaline earth carbonate and measured after drying at 105
5 °C for 3h in an oven until the weight is constant. If the water content is higher than 5 wt.-%, the sieving and/or classification step in the production of the alkaline earth carbonate particles might be negatively influenced.

The natural alkaline earth carbonate particles are preferably produced by dry
10 crushing, dividing and/or grinding in a hammer mill to a top cut size of 99 wt.-% < 7 mm.

The grinding may be performed in any other known grinding equipments with which those skilled in the art are familiar for the coarse grinding of natural alkaline earth
15 carbonate. For example, conventional ball mills, autogenous or non-autogenous milling, are suitable for dry grinding the alkaline earth particles used in the present invention.

In view of the fact that the content of fines should be as low as possible in order to
20 avoid dusting, combinations of such mills or combinations of one or more such mills with cyclones and sieves are most suitable.

Screening with a sieve or screen, such as a metal screen, is most preferred for reducing fines, as well as air fractionation by centrifugal force such as in a cyclone
25 and/or selector. Optionally, fines are washed off or extracted with a non-reacting liquid such as water.

For example, for obtaining marble particles having the desired particle size, marble pieces may be comminuted in a hammer mill to a particle size of not more than 7 mm
30 followed by screening at 0.5 mm. The fine fraction is treated by air cyclone and/or an

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air selector to reduce most of the fines having a particle size of smaller than 0.05 mm, better most of the fines < 0.09 mm or 0.1 mm.

It is preferred that, after the comminution step, the alkaline earth carbonate powder
5 obtained can be further classified by sieving using well known standard screens of defined mesh size for example as described in ISO 787/7.

The classification preferably provides the following fineness:

- 10 - the residue on a 500 μm sieve preferably is ≤ 10 wt.-%, more preferably ≤ 8 wt.-%, most preferably ≤ 5 wt.-%, e.g. 3 to 4 wt.-%, and/or
- the residue on a 200 μm sieve preferably is from 20 to 60 wt.-%, more preferably from 25 to 50 wt.-%, most preferably from 30 to 40 wt.-%, e.g. 35 wt.-%; and/or
- the residue on a 90 μm sieve preferably is from 50 to 95 wt.-%, more preferably
15 from 70 to 92 wt.-%, especially from 73 to 90 wt.-%, e.g. 80 wt.-%; and/or
- the residue on a 45 μm sieve preferably is ≥ 90 wt.-%, more preferably ≥ 93 wt.-%, most preferably ≥ 95 wt.-%, especially from 97 to 99 wt.-%, e.g. 98 wt.-%.

It is especially preferred that from 50 to 80 wt.-%, preferably from 60 to 80 wt.-%,
20 e.g. 65 wt.-% of the natural alkaline earth carbonate particles have a particle size of between 90 to 500 μm .

The median particle diameter of the natural alkaline earth carbonate particles preferably is from 110 to 400 μm , more preferably from 130 to 300 μm , particularly
25 from 135 to 200 μm , most preferably from 137 to 165 μm , e.g. from 142 to 165 μm measured according to the screening method using ISO screens of defined size. The results are drawn into a xy-graph.

By the use of natural alkaline earth carbonate such as natural marble, no
30 agglomeration or precipitation steps are needed for obtaining particles having an

effective size and form in dry blast cleaning, thus providing a more economic and ecologic way of cleaning solid surfaces by dry blasting.

5 Cleaning in the sense of the present invention means the removal of any kind of coatings from solid surfaces by the treatment with alkaline earth carbonate according to the present invention. Coatings which can be removed are e.g. selected from the group comprising paints, food residues such as e.g. milk or chocolate, pharmaceutical residues in containers or vessels, oils and tar substances, gas condensates, etc.

10

By the process according to the invention many kinds of solid surfaces can be cleaned, e.g. surfaces comprising materials selected from the group comprising steel, glass, wood and concrete.

15 Due to the special form and size of the alkaline earth carbonate particles it is possible to clean the surfaces very effectively without damaging the surface.

Thus, it is especially advantageous to use the process of the present invention in the field of food, oil, pharmaceutical and chemical industry, where there is a continuous
20 need for effective cleaning of production or reaction vessels. However, it can also be used for removing paint such as graffiti or weathering or air pollution products such as soot from walls.

According to the process of the invention there is generally no restriction with
25 respect to the angle with which the alkaline earth carbonate is blasted against the surface. It is preferred that the angle of incidence of the alkaline earth carbonate particles relative to the surface to be cleaned is from 1 to 90°, preferably 30 to 90°, more preferably 40 to 90°, e.g. 45°. Good results can also be achieved at an angle of more than 60° to 90°.

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- 10 -

For the blasting operation any blasting equipment suitable for dry blasting can be used, such as for example a sand blasting gun of the "STAR" type supplied by the company ASTURO, Assago, Italy.

- 5 The compressed air pressure may be from 0.5 to 250 bar, preferably 1 to 7 bar, more preferably 2 to 6 bar, e.g. 5 bar.

In this respect, any commonly employed nozzles can be used, e.g. having a round or elliptic, square or rectangular shape. Preferably the nozzle is made of metal, glass or
10 plastic, particularly of rubber gum.

Preferably the surface roughness (determined in μm depth using a three-dimensional laser microscope of the type ZEISS LSM 5 Pascal + Imager.Z1m) of the solid surface before and after the treatment remains unchanged. In any case, the surface
15 roughness after the treatment according to the present invention is not more than twice as high than before, preferably not more than 1.5 times higher, more preferably not more than 1.2 times higher.

A further advantage of the process according to the present invention is that the
20 natural alkaline earth carbonate has very favourable characteristics with respect to dusting.

In view of the above advantages, the use of natural alkaline earth carbonate particles having a mean particle diameter of from 100 to 500 μm and a Mohs hardness of
25 below 4 for a process for cleaning solid surfaces as defined above is a further aspect of the invention, provided that the alkaline earth carbonate particles are not in the form of precipitates or agglomerates.

A further aspect of the present invention is the process for their production
30 comprising the steps of

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- dry crushing, dividing and/or grinding the natural alkaline earth carbonate, and
- screening the resulting particles for reducing the fines,
which is described in more detail above.

- 5 The following figures, examples and tests will illustrate the present invention, but are not intended to limit the invention in any way.

Description of the Figures:

- 10 Figure 1 is a stereomicroscopic picture of corundum particles of Example 1 at a magnification of 20 x.

Figure 2 is a stereomicroscopic picture of alkaline earth carbonate particles of Example 6 at a magnification of 20 x.

15

Figures 3 shows the particle size distribution curve of alkaline earth carbonate particles of example 6.

EXAMPLES:

20

The experiments were carried out with a sand blasting gun of the "STAR" type supplied by the company ASTURO, Assago, Italy using nozzles having a round and rectangular shape, respectively. The compressed air pressure was 5 bar. The distance between the nozzle and the test piece was about 5 cm (± 0.5 cm). The treated surface area was about 2500 ± 500 mm². The surface was examined before and after the treatment by means of an optical scanner. The surface roughness was determined using a three-dimensional laser microscope of the type ZEISS LSM 5 Pascal + Imager.Z1m. For determining the depth in μm , the root mean square deviation of all of the z-values was determined.

30

1. Comparative Examples

Comparative Example 1

- 5 Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
Coating: TiO_2 paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.
Treating medium: Corundum; particle size: 200 – 800 μm (see Figure 1);
Mohs hardness: 9
- 10 Nozzle used: 6 mm x 25 mm
Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)
Treating time: 30 s

Results:

- 15 Treated surface in mm^2 : 2262
Cleaned surface in mm^2 : 999
Ratio (treated surface/cleaned surface): 2.26
Surface roughness: 6.5 μm
- 20 Dusting during application: low

The results show that corundum, which is a rather sharp-edged abrasive aluminium oxide, is a very effective cleaning medium on hard surfaces like steel sheets.

25 Comparative Example 2

- Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
Coating: TiO_2 paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.

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- 5 Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy); median particle diameter: 10 μm (determined by the sedimentation method in an aqueous solution of 0.1 wt% $\text{Na}_4\text{P}_2\text{O}_7$ with a SedigraphTM 5100 of Micromeritics Instrument Corporation)
- Mohs hardness: about 3
- Nozzle used: 6 mm x 25 mm
- Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)
- 10 Treating time: 30 s

Results:

- Treated surface in mm^2 : 2500
- Cleaned surface in mm^2 : no determinable cleaning effect
- 15 Ratio (treated surface/cleaned surface): not determinable
- Surface roughness: not detectable
- Dusting during application: extreme; visibility strongly reduced
- Bulk Density: 0.67 g/ml
- (The bulk density was calculated by measuring the volume of 100 g of product in a
- 20 100 ml graduated beaker (1 ml graduation))

The results show that calcium carbonate particles having a relatively fine particle diameter such as 10 μm are not effective in cleaning solid surfaces.

25 **Comparative Example 3**

- Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
- Coating: TiO_2 paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.

- Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy); sieve fraction: 2000 – 3500 μm; median particle diameter: 2700 μm
 Mohs hardness: about 3
- 5 Nozzle used: 6 mm x 25 mm
 Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)

Results:

- Surface roughness: not detectable (particles too coarse to spray.)
- 10 Dust during application: not applicable, particles too coarse to spray
- Bulk Density: 1.55 g/ml
 (The bulk density was calculated by measuring the volume of 100 g of product in a
 15 100 ml graduated beaker (1 ml graduation))

The particles were too coarse to be sprayed; experiment was abandoned. Thus, also particles having a large diameter cannot be used effectively in blast cleaning.

20 **Comparative Example 4**

- Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
- Coating: TiO₂ containing paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.
- 25 Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy)
 Mohs hardness: about 3
 Median particle diameter: ≅ 700 μm

- 15 -

Particle size distribution (determined by sieving according to ISO 787/7):

> 1250 μm 2 wt.-%

< 500 μm 4 wt.-%

- 5 Nozzle used: 6 mm x 25 mm
 Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)
 Treating time: 30 s

Results:

10

Treated surface in mm^2 : 2712

Cleaned surface in mm^2 : 951

Ratio (treated surface/cleaned surface): 2.85

Surface roughness: 2.19 μm

- 15 Dusting during application: very low dusting

Bulk Density: 1.41 g/ml

(The bulk density was calculated by measuring the volume of 100 g of product in a 100 ml graduated beaker (1 ml graduation))

- 20 The results show that the cleaning effect using calcium carbonate particles having a diameter of 700 μm and the above mentioned particle size distribution are nearly as effective as corundum particles. Cleaning with these calcium carbonate particles provides for a much lower surface roughness, but still more than twice as much as surface roughness than the untreated material.

25

Comparative Example 5

Support: Sheet of glass

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Coating: Whole milk having a water content of about 87.5 wt-%, dried to a water content of about 3 wt-% in 12 hours in a drying oven at 110 °C.

Treating medium: Corundum; particle size: 200 – 800 µm
 5 Mohs hardness: 9

Nozzle used: Round; diameter: 10 mm

Angle of incidence: 45° relative to the surface

Treating time: 75 g of treating medium in about 10 s

10 **Results:**

Treated surface in mm²: ~ 4000

Cleaned surface in mm²: > 3000

Ratio (treated surface/cleaned surface): < 5.33

15 Surface roughness: strong damaging of the glass surface

Dust during application: little

The dried milk coating was completely removed; however the surface of the sheet of glass was strongly damaged, scratched and matt by the hard corundum particles
 20 (visually detectable at a distance of 15 to 30 cm).

2. Examples according to the Invention

Inventive Example 6

25

Treating medium: Natural calcium carbonate
 (marble from South Tyrol, Italy, containing 6 - 7 wt.-%
 dolomite (calculated by analysing the Mg content by ICP in
 HCl extract)); cf. Figure 2

30

Mohs hardness: about 3

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HCl insolubles: 2.7 wt%

Humidity: 0.08 to 0.12 wt.-%

Median particle diameter: 137 μm (cf. Figure 3)

Particle size distribution (determined by sieving according to
 5 ISO 787/7):

> 500 μm	3 wt.-%
> 200 μm	35 wt.-%
< 90 μm	30 wt.-%
< 45 μm	5 wt.-%

10

Test a)

Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm

Coating: TiO₂ paint comprising highly cross-linked
 15 polyester/acrylate/isocyanate as a binder.

Nozzle used: 6 mm x 25 mm

Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)

Treating time: 30 s

20 Results:

Treated surface in mm ² :	2327
Cleaned surface in mm ² :	276
Ratio (treated surface/cleaned surface):	8.44
25 Surface roughness:	1.5 μm
Dust during application:	little
Bulk density:	1.45

(The bulk density was calculated by measuring the volume of 100 g of product in a 100 ml graduated beaker (1 ml graduation))

The results of test a) show that the cleaning effect using calcium carbonate particles having a median diameter of 137 μm and the above mentioned particle size distribution are not as effective as with corundum particles. However cleaning with calcium carbonate particles according to the invention is much smoother with respect to the surface to be cleaned

Test b)

- 10 Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
 Coating: Whole milk having a water content of about 87.5 wt-%, dried to a water content of about 3 wt-% in 12 hours in a drying oven at 110 °C.
 Nozzle used: 6 mm x 25 mm
 15 Angle of incidence: 45° relative to the surface
 Treating time: 30 s

Results:

- 20 Treated surface in mm^2 : 500
 Cleaned surface in mm^2 : > 400
 Ratio (treated surface/cleaned surface): < 1.25
 Surface roughness: 1.0 - 1.2 μm
 Dust during application: little

25

The results of test b) show that the cleaning effect using calcium carbonate particles having a median diameter of 137 μm and the above mentioned particle size distribution are only slightly less effective as with corundum particles. However cleaning with calcium carbonate particles according to the invention is much

smoother with respect to the surface to be cleaned. The surface roughness is nearly unchanged.

Test c)

5

Support: Plate of window glass

Coating: Whole milk having water content of about 87.5 wt.%, dried to a water content of about 3 wt.% in 12 hours in a drying oven at 110 °C.

10 Nozzle used: 6 mm x 25 mm

Angle of incidence: 45° relative to the surface

Treating time: about 30 s

Results:

15

The dried milk coating was completely removed; while the glass surface remained intact (no haze detectable visually at a distance of 15 to 30 cm).

Dust during application: little

20

Inventive Example 7

Support: Stainless sheet steel (V2A), surface roughness: 1.0 µm

Coating: TiO₂ paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.

25

Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy; cf. Example 6 washed to reduce fines < 45 µm

Mohs hardness: about 3

30

Humidity: 0.08 to 0.12 wt.-%

- 20 -

Median particle diameter: 142 μm

Particle size distribution (determined by sieving according to ISO 787/7):

5	> 500 μm	3 wt.-%
	> 200 μm	35 wt.-%
	< 90 μm	27 wt.-%
	< 45 μm	2 wt.-%

10	Nozzle used:	6 mm x 25 mm
	Angle of incidence:	90° relative to the surface (i.e. perpendicular to the surface)
	Treating time:	30 s

Results:

15	Treated surface in mm^2 :	2186
	Cleaned surface in mm^2 :	418
	Ratio (treated surface/cleaned surface):	5.23
	Surface roughness:	1.2 μm
20	Dust during application:	very little
	Bulk density:	1.50

(The bulk density was calculated by measuring the volume of 100 g of product in a 100 ml graduated beaker (1 ml graduation))

25 Even less dust was observed during surface cleaning compared with the unwashed sample of Example 6 a). Furthermore the results show that the cleaning effect using calcium carbonate particles having a median diameter of 142 μm and the above mentioned particle size distribution are more effective as with the calcium carbonate particles of Example 6, achieving the same or even better surface roughness of the

solid surface after cleaning, i.e. effective cleaning at low dusting and very low surface damage is possible with the inventive process.

Inventive Example 8

- 5
- Support: Stainless sheet steel (V2A), surface roughness: 1.0 μm
- Coating: TiO_2 paint comprising highly cross-linked polyester/acrylate/isocyanate as a binder.
- 10 Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy)
- Mohs hardness: about 3
- Humidity: 0.08 to 0.12 wt.-%
- Median particle diameter: 200 μm
- 15 Particle size distribution (determined by sieving according to ISO 787/7):
- | | |
|---------------------|----------|
| > 500 μm | 4 wt.-% |
| > 200 μm | 50 wt.-% |
| < 90 μm | 8 wt.-% |
| < 45 μm | 1 wt.-% |
- 20 Nozzle used: 6 mm x 25 mm
- Angle of incidence: 90° relative to the surface (i.e. perpendicular to the surface)
- Treating time: 30 s

Results:

- 25
- | | |
|--|-------------------|
| Treated surface in mm^2 : | 2908 |
| Cleaned surface in mm^2 : | 2414 |
| Ratio (treated surface/cleaned surface): | 1.21 |
| Surface roughness: | 1.4 μm |

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Dust during application: very little

The results show that the sample having a median diameter of 200 μm and a high weight fraction of between 200 to 500 μm provide even better results with respect to cleaning efficiency and low dusting compared with the samples with a median diameter of 137 and 142 μm , respectively. The surface roughness is about the same.

Inventive Example 9

- 10 Support: Plate of glass
- Coating: Whole milk having a water content of about 87.5 wt.-%, dried to a water content of about 3 wt.-% in 12 hours in a drying oven at 110 °C.
- 15 Treating medium: Natural calcium carbonate (marble containing dolomite from South Tyrol, Italy)
- Mohs hardness: about 3
- Humidity: 0.08 to 0.12 wt.-%
- Median particle diameter: 200 μm (see Figures 3 to 5)
- Particle size distribution (determined by sieving according to ISO 787/7):
- 20 > 500 μm 4 wt.-%
- > 200 μm 50 wt.-%
- < 90 μm 8 wt.-%
- < 45 μm 1 wt.-%
- 25 Nozzle used: 6 mm x 25 mm
- Angle of incidence: 45° relative to the surface
- Treating time: 23 g treatment agent in about 10 s

Results:

The dried milk coating was completely removed; while the glass surface remained
5 intact (no haze detectable visually at a distance of 15 to 30 cm).

Dust during application: little

Claims

1. A process for cleaning solid surfaces by dry blasting said surfaces with natural alkaline earth carbonate particles having a mean particle diameter of
5 from 100 to 500 μm and a Mohs hardness of below 4, provided that the alkaline earth carbonate particles are not in the form of precipitates or agglomerates.
2. The process according to claim 1,
characterized in that the natural alkaline earth carbonate is natural calcium
10 carbonate and/or natural calcium magnesium carbonate.
3. The process according to any one of claims 1 or 2,
characterized in that the natural alkaline earth carbonate is selected from the group
comprising marble, calcite, chalk and dolomite, limestone and mixtures thereof.
15
4. The process according to any one of the preceding claims,
characterized in that the natural alkaline earth carbonate has an average Mohs
hardness of from 2.6 to 3.9, preferably from 2.6 to 3.4, e.g. 3.
- 20 5. The process according to any one of the preceding claims,
characterized in that the natural alkaline earth carbonate is marble, preferable
marble containing dolomite.
6. The process according to any one of the preceding claims,
25 **characterized in that** the alkaline earth carbonate content in the natural alkaline
earth carbonate mineral is > 90 wt.-%, more preferably 95 to 99.9 wt.-%, e.g. 99.5
wt.-%.

- 25 -

7. The process according to any one of the preceding claims,
characterized in that the natural alkaline earth carbonate has a calcium content of at least 21 wt.-%, preferably > 35 wt.-%, more preferably > 38 wt.-%.

5 8. The process according to any one of the preceding claims,
characterized in that the natural alkaline earth carbonate has a magnesium content of maximum 13 wt.-%, preferably < 3 wt.-%, more preferably < 1.5 wt.-%.

9. The process according to any one of the preceding claims,
10 **characterized in that** the natural alkaline earth carbonate comprises dolomite in a content of 0.1 to 100 wt.-%, preferably from 2 to 10 wt.-%, more preferably from 3 to 7 wt.-%, e.g. 5 wt.-%.

10. The process according to any one of the preceding claims,
15 **characterized in that** the natural alkaline earth carbonate is classified providing a residue on a 500 µm sieve of ≤ 10 wt.-%, preferably ≤ 8 wt.-%, more preferably ≤ 5 wt.-%, e.g. 3 to 4 wt.-%.

11. The process according to any one of the preceding claims,
20 **characterized in that** the natural alkaline earth carbonate is classified providing a residue on a 200 µm sieve of from 20 to 60 wt.-%, preferably from 25 to 50 wt.-%, more preferably from 30 to 40 wt.-%, e.g. 35 wt.-%.

12. The process according to any one of the preceding claims,
25 **characterized in that** the natural alkaline earth carbonate is classified providing a residue on a 90 µm sieve of from 50 to 95 wt.-%, more preferably from 70 to 92 wt.-%, especially from 73 to 90 wt.-%, e.g. 80 wt.-%.

13. The process according to any one of the preceding claims,
30 **characterized in that** the natural alkaline earth carbonate is classified providing a

residue on a 45 μm sieve of ≥ 90 wt.-%, more preferably ≥ 93 wt.-%, most preferably ≥ 95 wt.-%, especially from 97 to 99 wt.-%, e.g. 98 wt.-%.

14. The process according to any one of the preceding claims,
5 **characterized in that** from 50 to 80 wt.-%, preferably from 60 to 80 wt.-%, e.g. 65 wt.-% of the natural alkaline earth carbonate particles have a particle size of between 90 to 500 μm .

15. The process according to any one of the preceding claims,
10 **characterized in that** the natural alkaline earth carbonate particles have a median particle diameter of from 110 to 400 μm , more preferably from 130 to 300 μm , particularly from 135 to 200 μm , most preferably from 137 to 165 μm , e.g. from 142 to 160 μm .

15 16. The process according to any one of the preceding claims,
characterized in that the natural alkaline earth particles are obtained by dry grinding, e.g. in a ball mill or hammer mill.

17. The process according to claim 16,
20 **characterized in that** the natural alkaline earth particles are obtained by a combination of one or more of such mills with cyclones and sieves.

18. The process according to any one of the preceding claims,
characterized in that the material to be removed from the solid surfaces is selected
25 from the group comprising paints, food residues such as e.g. milk or chocolate, and pharmaceutical residues.

19. The process according to any one of the preceding claims,
characterized in that the solid surfaces comprising materials selected from the
30 group comprising steel, glass, wood, and concrete.

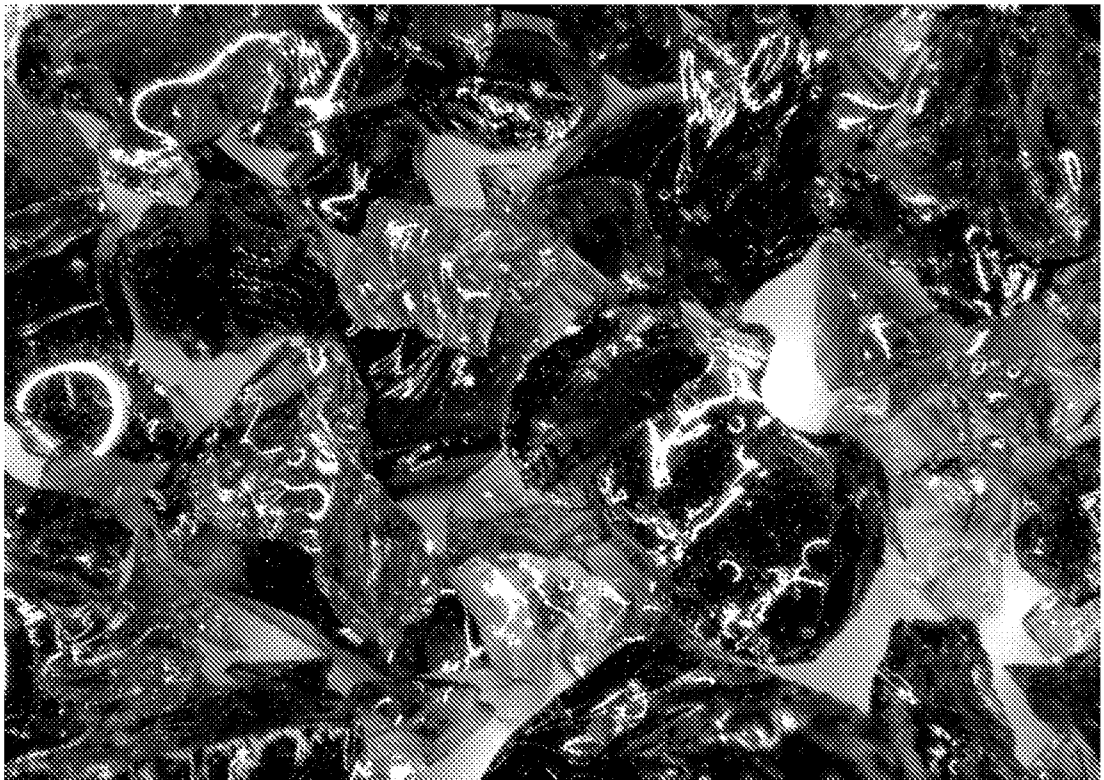
20. The process according to any one of the preceding claims, characterized in that the angle of incidence of the alkaline earth carbonate particles relative to the surface to be cleaned is from 1 to 90°, preferably 30 to 90°, more
5 preferably 40 to 90°, e.g. 45°, especially preferably more than 60 to 90°.

21. Use of natural alkaline earth carbonate particles for a process for cleaning solid surfaces according to any one of claims 1 to 20.

10 22. Process for the manufacture of natural alkaline earth carbonate particles having a median particle diameter of from 100 to 500 μm and a Mohs hardness of below 4 for the use in the process according to any one of claims 1 to 20, characterized by the steps of
- dry crushing, dividing and/or grinding the natural alkaline earth carbonate,
15 - screening the resulting particles for reducing the fines.

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Figure 1

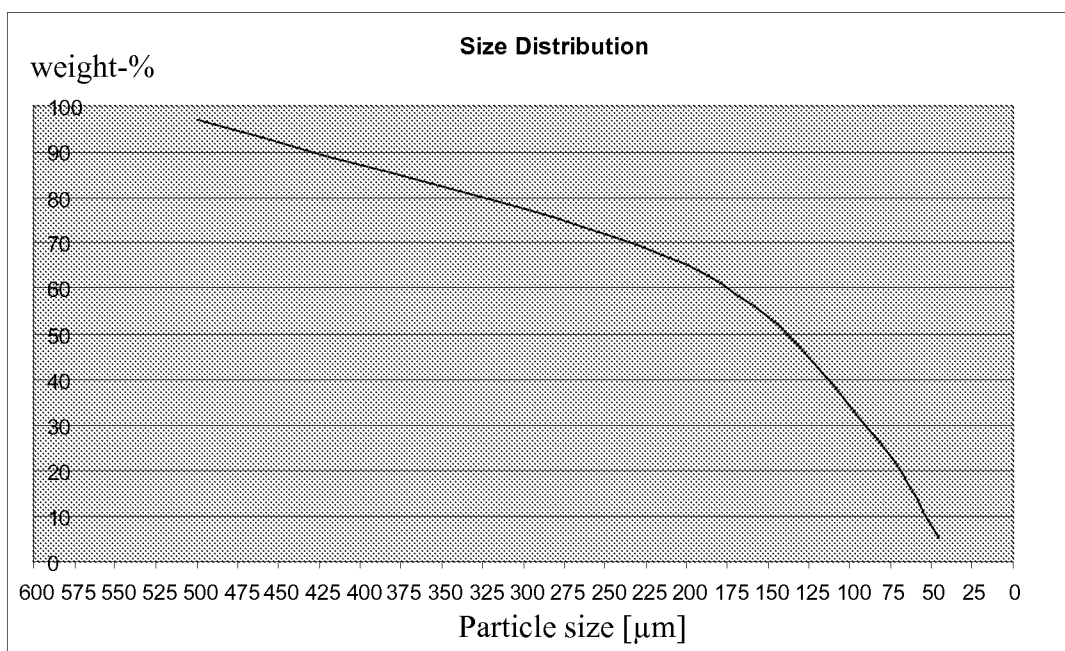


2/3

Figure 2



Figure 3



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/055273

A. CLASSIFICATION OF SUBJECT MATTER INV. B24C11/00		
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) B24C		
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 practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94/07658 A (NORSK HYDRO AS [NO]; MUELLER UDO [NO]; LARSEN ODDBJORN STEEN [NO]) 14 April 1994 (1994-04-14)	1-21
Y	page 1, paragraph 1 page 2, paragraph 3 page 5, paragraph 5 page 6, paragraph 1 claim 6	22
X	----- US 5 509 971 A (KIRSCHNER LAWRENCE [US]) 23 April 1996 (1996-04-23)	1-21
Y	column 3, lines 15-28, 45-49 column 4, lines 6-42 column 5, lines 7-18 claims 1,7 abstract ----- -/--	22
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance	*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	
E earlier document 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	*&* document member of the same patent family	
P document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search <p style="text-align: center; font-weight: bold;">28 July 2009</p>	Date of mailing of the international search report <p style="text-align: center; font-weight: bold;">05/08/2009</p>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center; font-weight: bold;">Eder, Raimund</p>	

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 97/41975 A (CHURCH & DWIGHT CO INC [US]) 13 November 1997 (1997-11-13)	1-21
Y	page 8, lines 24-30 page 9, lines 22-30 page 11, lines 2-6 page 15, line 27 - page 17, line 12 abstract	22
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