Detergent granules and a process for their preparation.

Detergent powders built with alkali metal carbonate and containing both sodium silicate and a calcium carbonate seed crystal material such as calcite are prepared by granulating a carbonate/silicate base powder with the seed crystal material, ideally in the presence of a liquid binder such as sucrose solution.
DESCRIPTION

DETERGENT GRANULES AND A PROCESS FOR THEIR PREPARATION

TECHNICAL FIELD OF INVENTION

The present invention is concerned with a process for the production of detergent granules built with alkali metal carbonate and containing a water-insoluble seed crystal material, such as calcite, for the alkali metal carbonate. Such products are useful especially for the domestic laundering of fabrics.

BACKGROUND AND PRIOR ART

Detergent compositions usually contain, in addition to a detergent active material, a detergency builder whose role, inter alia, is to remove hardness ions from the wash liquor which would otherwise reduce the efficiency of the detergent active material. Water-soluble phosphate materials have been extensively used as detergency builders. However for a number of reasons, including eutrophication allegedly caused by phosphates and cost, there has been a desire to use alkali metal carbonates, especially sodium carbonate, instead. Alkali metal carbonate detergency builders suffer however from a number of disadvantages. Firstly, the reaction between the alkali metal carbonate and calcium ions which are present in hard water results in the formation of water-insoluble calcium carbonate which, depending on the conditions, may be in such a form as to become deposited on the washed fabrics. Secondly, the reaction between the alkali metal carbonate and the calcium ions of the water is slow, especially at low temperatures, and is readily inhibited by materials which act as calcium carbonate precipitate growth inhibitors, referred to herein as poisons. The result of this is that the concentration of calcium ions in the wash liquor is not reduced as far or as fast as desired, so that some free calcium ions are still available to reduce the efficiency of the detergent active material.

As a possible solution to this problem it has been proposed to include in the detergent composition a water-insoluble material which can act as a seed crystal for the precipitating calcium carbonate and can absorb the poisons from the wash liquor. Among other materials, finely divided high surface area calcite has been proposed as such a material: see GB 1 437 950 (Unilever) and the corresponding US 4076653 (Davies et al).

However, the inclusion of calcite in detergent compositions is hampered by its physical form. One might consider putting small particle size calcite in a slurry together with other ingredients for spray-drying, but we have found that where alkali metal silicates are included this process leads to a loss of calcite seed activity. Calcite having a large surface area is required for maximum seed activity, but generally such material has a relatively small particle size, is dusty and is therefore difficult to handle. One alternative is to handle the calcite in a slurry, without drying to a powder, but this could also involve high storage and transport costs. It is therefore necessary to granulate the calcite, for example by conventional techniques of pan granulation or spray-drying, and to keep any silicate away from the calcite. The term "granulation" is used herein to mean any process of agglomerating fine particles into granules of a suitable size for incorporation into, or use directly as, detergent compositions.

Granulation of the calcite with a suitable binding agent has been proposed, for example, in GB 1 515 273 (Unilever). However, in order to be effective in its intended role in the wash liquor, it is necessary for the calcite to disperse rapidly when the product is added to water. Binding agents have generally been found seriously to reduce the dispersibility of the calcite. Attempts to granulate calcite with materials known to be good dispersing agents, for example some nonionic detergent active materials, have also been unsuccessful. The resulting granules may not have the necessary mechanical strength to solve the handling problems of the calcite. The problem is further complicated by the fact that some binding agents and dispersing agents proposed in the prior art are themselves poisons and will therefore reduce the seed activity of the calcite, thereby further adding to the problems which the calcite is intended to solve.

GB 2 174 712A (Unilever) discloses silicate-free detergent granules comprising a seed crystal such as calcite, a non-soap detergent-active material (preferably anionic) and a sugar. The preferred sugar is sucrose.

The granules are typically prepared by spraying a mixture of detergent-active material, water and sucrose onto calcite particles in a granulator. Alternatively they may be prepared by spray-drying. The granules are then dry-mixed with a detergent base powder containing other desired ingredients, notably sodium silicate; this might, for example, be a spray-dried base powder. If desired the calcite granules may contain other ingredients, notably sodium sulphate or sodium carbonate, but not sodium silicate.

The detergent powders prepared by this method contain separate calcite and silicate granules and, unless measures are taken to control their relative densities and particle sizes, segregation of the powder during storage and transport may occur. Such powders may also be more expensive to prepare by this method.

It has now been found that it is possible to prepare detergent products containing a detergent active, sodium carbonate, sodium silicate and calcite by a process which avoids the risk of such segregation.

DEFINITION OF THE INVENTION

According to the present invention there is provided detergent granules comprising at least: (I) a detergent active material; (ii) an alkali metal carbonate

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The detergent granules of the invention may further comprise a water-soluble or water-dispersible binder material which serves to adhere the seed crystal to the base powder. The binder material may be constituted by further detergent active material.

The invention further provides a process for the preparation of detergent granules comprising the steps of:

(a) granulating a composition comprising:

(i) a detergent active material
(ii) an alkali metal carbonate, and

(iii) an alkali metal silicate to form a granulated base powder and then

(b) granulating the granulated base powder formed in step (a) with a water-insoluble particulate carbonate which is a seed crystal for calcium carbonate and which has a surface area of at least 10 m²/g to cause the seed crystal to adhere to the surface of said base powder.

We are aware of Japanese Patent publication 60/262895 (Lion Co., Ltd.) which is directed to improving the flow properties of granular compositions containing detergent active materials, alkali metal silicate and alkali metal carbonate by adhering on the surface thereof small amounts of cubic calcium carbonate particles having a primary particle diameter of 0.1 to 1.5 microns. Such calcium carbonate material has an insufficient surface area for use as an effective seed crystal in the context of the present invention.

We are also aware of GB 1583081 (Unilever) which describes a process comprising contacting an alkali metal carbonate in particulate form with a liquid or pasty detergent active compound and admixing calcium carbonate powder so that the calcium carbonate adheres to the alkali metal carbonate particles. Such a process was said to prevent interaction between the alkali metal carbonate and the calcium carbonate, which interaction was believed to have a negative effect upon detergency. If conventional or high levels of detergent active are used in such a method, the resulting product may suffer from unacceptable physical properties.

In contrast, the present invention requires that the detergent active, the alkali metal carbonate and the alkali metal silicate constitute a common granulated base powder to which the seed crystals are adhered.

DESCRIPTION OF THE INVENTION

The detergent granules built with alkali metal (preferably sodium) carbonate, alkali metal silicate and a seed crystal material, preferably calcite, are prepared by a process comprising the two steps of granulation. A granulated base powder containing the components other than the calcite is first prepared. The base powder is then granulated with calcite, preferably in the presence of a liquid binder, as will be discussed in more detail below.

Detergent products prepared in accordance with the invention consist essentially of agglomerate particles composed of base powder and seed crystal material, held together, preferably by means of a binder. Of course other solid materials added by postdosing may also be present as discrete particles.

The base powder may be prepared by spray-drying an aqueous slurry containing all desired ingredients sufficiently heat-insensitive to be processed in this manner, other than the seed crystal material. These ingredients include not only the alkali metal carbonate material, the alkali metal silicate, and the detergent active material but may also include other detergency builders, fluorocarbons, antiredeposition agents such as sodium carboxymethyl cellulose, and salts such as sodium sulphate.

Alternatively the base powder may be made by marumerising or by non-slurry granulation, such as by pan granulation. These techniques are well known in the art and need no further description.

THE ALKALI METAL CARBONATE

An essential ingredient of the base powder used in the process of the invention is an alkali metal carbonate builder salt, preferably sodium carbonate.

The sodium carbonate typically amounts to from 20 to 80% by weight of the base powder, and the base powder often constitutes from 30 to 70% by weight of the final product, so the amount of sodium carbonate in the final composition will be correspondingly less, i.e. from 5% to 56% of the final product.

If desired, other builders may also be present to supplement the sodium carbonate, provided that they do not inhibit calcium carbonate crystal growth. Examples of suitable supplementary builders include citrates, nitrilotriacetates and soaps.

THE ALKALI METAL SILICATE

A further essential ingredient of the base powder is an alkali metal silicate. Sodium silicate is an important ingredient of spray-dried detergent compositions. It helps to give structure to the spray-dried powder and in the wash liquor it prevents the corrosion of metal surfaces of the washing machine. It is an advantage of the process of the invention that sodium silicate can be included in the base powder without the problem of calcite deactivation.

The alkali metal silicate is particularly sodium neutral, alkaline, meta- or orthosilicate. A low level of silicate,
for example 5-10% by weight of the final composition is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines. Lower levels eg. 2% to 5% may provide beneficial structuring of the powder. If higher levels of silicate are used up to a practical maximum of 30%, for example from 10% to 20% by weight, there can be a more noticeable improvement in detergency, which may permit some decrease in the water-soluble carbonate material content. This effect appears to be particularly beneficial when the products are used in water with appreciable levels of magnesium hardness. The amount of silicate can also be used to some extent to control the equilibrium pH of the wash liquor, which is generally within the range of 9-11, preferably 10-11 for an aqueous solution of the composition at the recommended concentration. It should be noted that higher pH (ie over pH10.5) tends to be more efficient as regards detergency, but it may be less desirable for domestic safety. Sodium silicate is commonly supplied in concentrated aqueous solution, but the amounts are calculated on an anhydrous basis.

THE DETERGENT ACTIVE MATERIAL

The granulated base powder also includes one or more detergent active materials, such as anionic and/or nonionic surfactants.

Anionic surfactants are well-known to those skilled in the detergents art. Examples include alkylbenzene sulphonates, particularly sodium linear C6–C15 alkylbenzene sulphonates; primary and secondary alkyl sulphates, particularly sodium C12–C15 primary alkyl sulphates; olefin sulphonates; alkane sulphonates; and fatty acid ester sulphonates.

Nonionic surfactants that may be used include primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol.

The base powder may also contain one or more soaps of fatty acids. The preferred soaps are sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow or sunflower oil.

The total amount of detergent-active material (surfactant), excluding soap, in the base powder may suitably range from 10 to 60% by weight: in a fully formulated product containing perhaps 30 to 70% by weight of base powder the amount will be correspondingly less i.e. from 3% to 42% of the final product. For low-sudsing powders intended for use in European drum-type automatic washing machines the weight ratio of anionic surfactant to nonionic surfactant in the final product preferably does not exceed 10:1, and more preferably does not exceed 8:1, but it should be remembered that nonionic surfactant may be sprayed on or postdosed on a carrier rather than included in the base powder, so that the ratio in the base powder may be higher, or indeed infinite. Medium-sudsing or high-sudsing products tend to have a higher ratio, and nonionic surfactant may be omitted altogether from such products.

THE SEED CRYSTAL

In the process of the invention, the base powder is granulated with a particulate water-insoluble carbonate capable of acting as a seed crystal for the precipitate which results from the reaction in the wash liquor between calcium water-hardness ions and the water-soluble carbonate builder salt present in the base powder. Thus this water-insoluble particulate material is a seed crystal for calcium carbonate, and is preferably itself a crystal form of calcium carbonate.

The water-insoluble particulate carbonate material should be finely divided, and should have a surface area of at least 10 m²/g, and preferably at least 15 m²/g. The particularly preferred material has surface area from 30-100 m²/g. Insoluble carbonate material with surface areas in excess of 100 m²/g may be used, if such materials are economically available.

Surface area is measured by nitrogen adsorption using the standard Bruauer, Emmet & Teller (BET) method. A suitable machine for carrying out this method is a Carlo Erba Sorpty (Trade Mark) 1750 instrument operated according to the manufacturer’s instructions.

It is most preferred that the high surface area material be prepared in the absence of poisons, so as to retain its seed activity.

The insoluble carbonate material will usually have an average particle size of less than 10 microns, as measured by conventional techniques.

When the insoluble carbonate material is calcium carbonate, any crystalline form thereof may be used or a mixture thereof, but calcite is preferred as aragonite and vaterite are less readily available commercially, and calcite is a little less soluble than aragonite or vaterite at most usual wash temperatures. When any aragonite or vaterite is used it is generally in admixture with calcite. In the following general description, the term "calcite" is used to mean either calcite itself or any other suitable water-insoluble calcium carbonate seed material.

The amount of calcite in a final powder prepared in accordance with the Invention is preferably at least 5%, such as up to 40% by weight, more preferably from 10 to 30% by weight.

OPTIONAL INGREDIENTS

Many detergent compositions also contain a bleach, to bleach stains and assist in the removal thereof from fabrics. Peroxybleaches which generate hydrogen peroxide in solution, such as sodium perborate, have been used for this purpose but are not especially effective at low temperatures. Products capable of bleaching at lower temperatures contain peracid generating systems which may comprise a peracid itself or, more commonly, a mixture of peroxybleach and an activator therefor, such as sodium perborate together with...
tetraacetylethylene diamine (TAED). The performance of such systems is especially sensitive to the presence of low levels of transition metal ions, which are often present in small amounts in raw materials used for preparing the compositions. It has been proposed therefore to include in such compositions materials such as the salt of a polymethylene phosphonic acid, generally available under the Trade Mark DEQUEST, and described in British patent specification GB 2 048 930 (UNILEVER) and the corresponding US 4259200 (Heslam et al). These materials stabilise the peracid bleach system against the effect of transition metals, but since Dequest is itself a phosphorus containing material it has been thought desirable to exclude Dequest from detergent compositions not containing phosphate builders.

The use of a sodium carbonate/calcite builder mixture in place of sodium tripolyphosphate leads to a number of differences, including higher alkalinity in the wash liquor. It is known that the bleaching performance of peracetic acid (generated from a mixture of sodium perborate and TAED) is reduced at a higher pH and this, together with the absence of Dequest to stabilise the peracetic acid from the effects of transition metals would lead one to expect that the bleach performance of a phosphorus free composition based on a sodium carbonate/calcite mixture would be significantly reduced in comparison with its phosphate containing equivalent.

We have now discovered however that the performance of such compositions is substantially better than might have been predicted and in some cases a benefit occurs relative to an equivalent phosphate containing composition.

The peracid generating bleach system may be selected from peracids themselves, or a mixture of a peroxybleach such as an inorganic persalt and a peracid bleach activator. The activator makes the bleaching more effective at lower temperatures, ie. in the range from ambient temperature to about 60°C. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator therefor is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound. Whilst the amount of the bleach system, ie. peroxybleach compound and activator may be varied between about 5% and about 35% by weight of the detergent compositions, it is preferred to use about 9% to about 30% of the ingredients forming the bleach system.

Typical examples of suitable peroxybleach compounds are alkali metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persulphates and persilicates of which sodium perborate is preferred. The peroxybleach compound is normally added in separately to the detergent base powder.

We have found that the present invention is especially applicable when the peroxybleach compound is sodium perborate monohydrate, especially such material which has a surface area in excess 5m²/g and a caking index, as described in European Patent Specification No. 164778 (UNILEVER - and the corresponding US 4650599 (Farnworth et al) above zero.

Activators for peroxybleach compounds have been amply described in the literature, including British patents 836 988, 855 735, 907 356, 907 358, 970 950, 1 003 310 and 1 246 339; US patents 3 332 882 and 4 128 494; Canadian patent 844 481 and South African patent 68/6 344.

The N-diacylated and N, N'-polyacylated amines are of special interest, particularly N, N', N'-tetraacetyl ethylene diamine (TAED).

It is preferred to use the activator in granular form, preferably wherein the activator is finely divided as described in British Patent Specification No. 2 053 998 (UNILEVER) - and the corresponding US 4283302 (Foret et al).

It is a feature of the invention that the products are preferably free of phosphorus. In particular, the products should contain less than about 0.01% polymethylene phosphonic acids and their salts, calculated as phosphonic acid.

Examples of other optional ingredients include the lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, fabric softening agents, such as quaternary ammonium salts and smectite clays, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants. Particularly when the composition does not contain an anionic detergent active material, it can be beneficial to include an anti-ashing material to reduce the deposition of calcium carbonate onto fabrics.

THE BINDER MATERIAL

The granulation of the base powder with the calcite may be carried out in the presence of a liquid binder, although if the base powder is in a tacky state when contacted with the calcite, the addition of a binder at this stage is not essential.

According to a preferred embodiment of the invention, the liquid binder is an aqueous solution of a sugar. By the term "sugar" is meant a mono-, di- or polysaccharide or a derivative thereof, or a degraded starch or chemically modified degraded starch which is water soluble. The saccharide repeating unit can have as few as five carbon atoms or as many as fifty carbon atoms consistent with water solubility. The saccharide derivative can be an alcohol or acid of the saccharide as described in Lehninger's Biochemistry (Worth, 1970). By "water-soluble" in the present context it is meant that the sugar is capable of forming a clear solution or a stable colloidal dispersion in distilled water at room temperature at a concentration of 0.01 g/l.

Amongst the sugars which are useful in this invention are sucrose, which is most preferred for reasons of...
availability and cheapness, glucose, fructose, maltose (malt sugar) and cellobiose and lactose which are disaccharides. A useful saccharide derivative is sorbitol.

If sucrose is the chosen sugar, it is preferably used in an amount corresponding to from 1 to 5% by weight of the final product, and the amount of water that enters the product by way of the sucrose solution is preferably from 2 to 10% by weight; these percentages are based on the ultimate, fully formulated product including any postdosed ingredients. Thus a relatively concentrated sucrose solution (1 to 3 parts of water per part of sucrose) is preferably employed. It may be necessary to evaporate off some water after spraying on the sucrose solution, rather than allowing all of it to remain as free moisture in the final product.

The use of sucrose as the binder has the advantage that no loss of calcite seed activity occurs.

Alternatively, the binder may comprise an aqueous solution containing a low level of an anionic polymer, for example, sodium carboxymethyl cellulose, which is not a calcite poison. Advantageously an aqueous solution containing both sugar and a low level of a suitable anionic polymer may be used; the final product is less dusty, albeit at the cost of a small loss of calcite seed activity. The amount of sodium carboxymethyl cellulose incorporated in the binder solution suitably corresponds to a level in the final product of from 0.01 to 0.1% by weight.

Another binder material that may be used in the process of the invention is a nonionic surfactant, for example, a C12-C15 primary alcohol ethoxylated with 3-10 moles of ethylene oxide. Nonionic surfactants may be used alone, in admixture or conjunction with water, or in admixture or conjunction with sugar solution. Nonionic surfactants used alone may if necessary be warmed to a temperature at which they are mobile liquids. When nonionic surfactants and sugar solutions are both used, it may be advantageous to apply them separately to avoid gelling problems.

THE GRANULATION STEP

The granulation step may be carried out using any suitable mixing apparatus, and may be carried out batchwise or continuously. The solid constituents (base powder and calcite) may be agitated together while the liquid binder or binders is or are sprayed on. A drying step may be required depending on the amount of water present in the liquid binder.

We have now discovered that calcite may successfully be incorporated by the use of a simple modification to a conventional single level spray-drying tower.

The process comprises:

(i) spray-drying an aqueous slurry comprising the detergent active material, the alkali metal carbonate, the alkali metal silicate and optionally other conventional detergent ingredients, in a spray-drying tower; and

(ii) simultaneously injecting the seed crystal material into the tower, whereby particles of the seed crystal material encounter within the tower particles formed by the drying of the aqueous slurry.

The calcite may be introduced in particulate form into the tower by any suitable method. Two suitable methods are known as "blow-in" and "screw-in". "Blow-in", as its name suggests, involves feeding the calcite to a hopper of an air pump which blows calcite through a pipe into the tower. "Screw-in" involves the use of a screw feeder. A less preferred method is to spray-in a calcite slurry, optionally containing a surfactant, such as an anionic surfactant to reduce viscosity.

Blowing in offers the advantage of flexibility with respect to the direction in which the calcite enters the tower.

The calcite may be blown in upwardly and vertically, downwardly and vertically, radially and horizontally, tangentially, or in any intermediate direction. In most spray-drying towers the detergent slurry is sprayed downwardly from nozzles situated in a upper region of the tower, and the calcite should be introduced at a level below that of the spray nozzles so that calcite particles will encounter base powder granules formed by drying of the slurry droplets. Advantageously, the calcite enters the tower at a level below that of the hot air inlet. Of course, in a multilevel tower slurry may be sprayed in at various levels and it is then possible for the calcite too to be injected at several different levels and/or in several different directions.

In a preferred embodiment of this process, the calcite is injected tangentially at a level below that of the hot air inlet, preferably in the cone of the tower.

Because the base powder slurry contains alkali metal silicate, any direct contact between the silicate in solution and the calcite will lead to loss of seed crystal activity of the latter, and it is therefore desirable that the slurry droplets should be sufficiently dry when they encounter the calcite particles. On the other hand, it is necessary that the base powder granules should not be too dry when they encounter the calcite particles, i.e. they must be tacky enough that the calcite particles adhere to the surface thereof. It follows therefore that the positioning of the calcite injection is critical. In a small (1.8 m diameter) tower, it has been found that the calcite should preferably be injected at a level and/or in such a direction that the calcite particles will come into contact with slurry droplets or granules at least about 4 metres below the spray nozzles; but different limits may be applicable to larger towers.

Finely divided high surface area calcite is a fine and dusty material and metering to the air pump or screw feeder may be difficult. It has been found that a variable speed volumetric screw feeder - the ACCU-RATE (Trade Mark) feeder, ex March Systems Ltd., Newbury, Berkshire - linked to a mechanically flexed mass flow hopper, will perform this task successfully.

If desired, other solid materials that are not to be incorporated via the slurry may be injected together with
the calcite, as an alternative to postdosing. This only applies, of course, to materials that are stable to the relatively high temperatures in the tower, and is not a suitable method for introducing such components as enzymes, bleaches or bleach precursors. One example of a material that may be introduced together with calcite is sodium bicarbonate.

To the agglomerated powder obtained in the granulation step there may be postdosed any required additives that cannot be incorporated in the base powder because of heat-sensitivity or adverse interactions with other slurry ingredients. Examples of such materials are bleaches, bleach activators, bleach stabilisers, enzymes, lather suppressors and perfumes.

Detergent compositions according to the invention combine maximum calcite seed activity with good powder properties.

DESCRIPTION OF DRAWINGS

Embodyments of the invention will now be described in greater detail, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 represents a first spray-drying tower adapted for preparing the granules of the invention;

Figure 2 represents a second spray-drying tower adapted for preparing granules of the invention.

Referring now to Figure 1 of the accompanying drawings, a spray-drying tower 1 is provided in its upper region with a downwardly directed spray nozzle 2 fed by a supply line 3. A ring main 4 through which drying air may be introduced is located in a lower region of the tower 1. A flexible pipe 5 connected to a solids feeder (not shown) via an air pump (not shown) enters the tower at a level below the ring main 4.

In preparing the granules of the invention, a detergent slurry is pumped along the line 3 to the nozzle 2 where it is atomised into droplets forming the shape of a cone indicated by the dotted lines 6. Hot air is forced into the tower and upwards through the ring main 4 and the falling droplets of slurry dry to form granules, which are initially tacky, as they fall through the tower. Solid finely-divided calcite is blown upwardly through the flexible pipe 5, the calcite particles encounter tacky granules of dried slurry and adhere thereto, and the composite particles fall to the base of the tower.

The tower shown is Figure 2 is used in a similar manner, differing only in that the solid calcite blown in through a flexible pipe 7 enters the tower at a higher level, above the ring main 4, so that the calcite granules have the opportunity to collide with wetter slurry granules.

In an alternative arrangement, differing from those of Figures 1 and 2, the solid calcite may be blown in through a flexible pipe which enters the tower tangentially, at a level substantially below the ring main 4, in the bottom cone of the tower.

EXAMPLES

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

Example 1 to 3

A spray-dried base powder was prepared to the following composition:
<table>
<thead>
<tr>
<th>Parts</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium linear alkylbenzene sulphonate (Dobane (Trade Mark) 113 ex Shell)</td>
<td>11.0</td>
</tr>
<tr>
<td>Nonionic surfactant 7EO (Synperonic (Trade Mark) A7 ex ICI)</td>
<td>4.0</td>
</tr>
<tr>
<td>Sodium soap (Pristerine (Trade Mark) 4910 ex Unichema)</td>
<td>2.5</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>30.0</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>0.55</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>6.0</td>
</tr>
<tr>
<td>Minor ingredients</td>
<td>0.3</td>
</tr>
<tr>
<td>Water</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>58.35</td>
</tr>
</tbody>
</table>

This was a crisp, free-flowing powder.
Four powders were prepared by mixing 58.35 parts of this base powder with 20 parts of calcite having a nominal surface area of 100 m²/g (Socal (Trade Mark) U3 ex Solvay) in a batch mixer.
One (Comparative Example A) was used as a control, and onto the other three were sprayed various liquid binders as specified below (in parts by weight):

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>6</td>
<td>2.45</td>
<td>6</td>
</tr>
</tbody>
</table>

The properties of the resulting powders were as follows:
Calcite seed activity (%) 100 100 100 68
Bulk density (g/litre) 385 443 382 432
Dynamic flow rate (ml/s) 52 86 67 92
Compressibility (% v/v) 19 20 22 21
Respirable dust (mg/100g) 3.2 0.4 0.27 0.07

It will be seen that the powder A consisting simply of calcite postdosed to base powder had a poor dynamic flow rate and was very dusty. The spray-on of sucrose solution (Example 1) improved both properties substantially. Use of sodium carboxymethyl cellulose solution (Example 2) improved the dustiness but the dynamic flow rate was not ideal. Use of sucrose/sodium carboxymethyl cellulose solution gave good powder properties and very low dustiness at the cost of a slightly reduced calcite seed activity.

Examples 4 to 7
A spray-dried base powder was prepared to the following composition:
This was a crisp, free-flowing powder.

Five powders were prepared by mixing 55.35 parts of this base powder with 20 parts of the calcite used in Examples 1 to 3, in a batch mixer. One powder (Comparative Example B) was used as a control, and onto the others were sprayed various liquid binders as shown in the Table, which also shows the properties of the resulting powders.

The nonionic surfactant 7EO used in Examples 4 and 5 was heated to about 50°C before spraying. The powders of Examples 5 and 7 were prepared as follows: first the nonionic surfactant (100% active matter) was sprayed on, followed by an aqueous sucrose solution (2 parts sucrose and 4 parts water).

The powders of Examples 5 and 7, containing nonionic surfactant, sucrose and water as binders, combined excellent powder properties, low dustiness and high calcite seed activity.
### Examples 4 to 7

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic surfactant 7EO</td>
<td>-</td>
<td>3</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nonionic surfactant 4EO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sucrose</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Calcite seed activity (%)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>71</td>
</tr>
<tr>
<td>Bulk density (g/litre)</td>
<td>354</td>
<td>344</td>
<td>380</td>
<td>365</td>
<td>357</td>
</tr>
<tr>
<td>Dynamic flow rate (ml/s)</td>
<td>nil</td>
<td>50</td>
<td>83</td>
<td>49</td>
<td>96</td>
</tr>
<tr>
<td>Compressibility (% v/v)</td>
<td>26</td>
<td>26.5</td>
<td>19</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Respirable dust (mg/100g)</td>
<td>6.9</td>
<td>5.9</td>
<td>0.2</td>
<td>4.7</td>
<td>0.27</td>
</tr>
</tbody>
</table>
Example 8
A slurry having a moisture content of 38-40% weight was prepared using the following ingredients:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight % (of powder)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branched alkylbenzene sulphonate, sodium salt</td>
<td>28.0</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>40.3</td>
</tr>
<tr>
<td>Anhydrous neutral sodium silicate</td>
<td>8.0</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>0.5</td>
</tr>
<tr>
<td>Fluorescer</td>
<td>0.2</td>
</tr>
<tr>
<td>Salts (from the alkylbenzene sulphonate)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>78.0</td>
</tr>
</tbody>
</table>

The slurry was spray-dried using the tower shown in Figure 1. Finely divided calcite of surface area 63 m²/g (Socal (Trade Mark) U3 ex Solvay et Cie) was blown in at a rate equivalent to a nominal level of 10% by weight in the formulation. The powder was spray-dried to a moisture content of about 8% by weight. 5% of sodium bicarbonate was then postdosed.

The final powder had the following properties:

- Actual calcite content (wt %) 7.5
- Actual moisture content (wt %) 8.3
- Bulk density (g/litre) 385
- Dynamic flow rate (ml/s) 87
- Compressibility (% v/v) 13

The powder properties were thus satisfactory.

The actual calcite content was measured by dissolving the powder in dilute hydrochloric acid, adjusting the pH to 10 with ammonia, and titrating with ethylenediaminetetraacetic acid.

The calcite seed activity of the powders was checked by means of a water softening test. 3.5g of powder were dissolved in 1 litre of 24°FH (all Ca) water containing 10 ppm of sodium tripolyphosphate to simulate the calcite-poisoning effect of the soil on a dirty laundry load. The solution was stirred for 20 minutes at ambient temperature; precipitated calcium salts were removed using a very fine millipore filter (0.1 µm); and the total soluble calcium level in the resulting filtrate was determined by atomic absorption spectroscopy. Powders giving values of 2°FH and below for the total soluble calcium concentration are regarded as acceptable; values of 1°FH and below indicate excellent powders.

The powder of Example 1 gave a total soluble calcium concentration of 0.95°FH, showing that its calcite had retained its seed crystal activity.

Example 9
A slurry having the same composition as that of Example 8 was spray-dried using the tower shown in Figure 2, calcite being blown in at a somewhat higher position in the tower. The powder had the following properties:

- Actual calcite content (wt %) 7.2
- Actual moisture content (wt %) 11.9
- Bulk density (g/litre) 352
- Dynamic flow rate (ml/s) 80
- Compressibility (% v/v) 34
- Total soluble Ca concentration (°FH) 2.38

The compressibility was inferior to that of the powder of Example 8. The water-softening properties were
also inferior, showing some loss of calcite seed activity.
The lower blow-in position used in Example 8 is thus to be preferred on both counts.

Examples 10 and 11
The procedure of previous Examples 8 and 9 was repeated, using the modification of the tower shown in
Figures 1 and 2 in which the calcite is blown tangentially into the bottom cone of the tower. The powders had
the following properties:

<table>
<thead>
<tr>
<th></th>
<th>Example 10</th>
<th>Example 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual calcite content (wt %)</td>
<td>6.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Actual moisture content (wt %)</td>
<td>11.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Bulk density (g/litre)</td>
<td>430</td>
<td>410</td>
</tr>
<tr>
<td>Dynamic flow rate (ml/s)</td>
<td>96</td>
<td>80</td>
</tr>
<tr>
<td>Compressibility (% v/v)</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>Total soluble Ca concentration (°FH)</td>
<td>0.9</td>
<td>1.05</td>
</tr>
</tbody>
</table>

The powders thus showed good physical properties and undiminished calcite seed crystal activity.
The powders prepared as described in Examples 1 to 11 may be converted into fully formulated products by
the subsequent addition of conventional ingredients, up to a total of 100 parts.

Claims

1. A granular detergent product comprising:
   (i) from 3% to 42% of a detergent active material selected from anionic detergent active materials,
   nonionic detergent active materials, nonionic detergent active materials and mixtures thereof;
   (ii) from 5% to 56% of sodium carbonate;
   (iii) from 5% to 30% of sodium silicate; and
   (iv) from 5% to 40% particulate calcite having a surface area of at least 10 m²/g;
   wherein said detergent active material, sodium carbonate and sodium silicate are in the form of
   granulated base powder, said calcite being adhered to the surface of said base powder.

2. A granular detergent product according to claim 1 further comprising a binder material which serves
to adhere said calcite to said base powder, said binder material being selected from sucrose, sodium
carboxymethyl cellulose and nonionic surfactants.

3. A granular detergent product according to claim 1 further comprising a peracid generating bleach
system selected from peracids and mixtures of a peroxybleach with a peracid bleach activator, the
product being essentially free of phosphorus.

4. A process for the preparation of a granular detergent product comprising
   (i) from 3% to 42% of a detergent active material selected from anionic detergent active materials,
   nonionic detergent active materials and mixtures thereof;
   (ii) from 5% to 56% of sodium carbonate;
   (iii) from 5% to 30% of sodium silicate; and
   (iv) from 5% to 40% particulate calcite having a surface area of at least 10 m²/g;
   comprising the steps of
   a) granulating said detergent active material, sodium carbonate and sodium silicate to form a
   granulated base powder; and
   b) granulating said granulated base powder with said calcite, to cause said calcite to adhere to the
   surface of said base powder.

5. A process according to Claim 4, wherein said granulated base powder is formed by spray-drying an
aqueous slurry comprising said detergent active material, sodium carbonate and sodium silicate in a
spray-drying tower.

6. A process according to claim 5, wherein said calcite is simultaneously injected into said spray-drying
tower, whereby calcite particles encounter said granulated base powder within said tower.