A high active detergent particle with Ra less than 6 µm obtainable by extruding surfactant blends with less than 5 wt%, inorganic structurant to make a hard extruded particle and coating the particle with 5 to 40 wt% soluble inorganic salt.
HIGH ACTIVE DETERGENT PARTICLES

This invention relates to high active detergent particles, in particular to high active detergent particles made from extruded surfactant blends and to compositions comprising a major part of such particles.

BACKGROUND AND PRIOR ART

To reduce the chemicals used in the laundry washing process it has been proposed to decrease the builder salts in laundry detergent formulations. Without other formulation changes, this reduction could adversely affect the performance of the composition in hard water. It has been proposed to ameliorate this problem by using surfactant blends that are tolerant of the presence of hardness ions in the wash water, in particular blends tolerant to calcium ions. These surfactant blends have been termed "calcium tolerant surfactant blends".

For the detergent formulator use of such calcium tolerant surfactant blends poses a new problem. Builder materials have often been included in the formulation not only to provide hard water detergency performance, but also to enable efficient manufacture of free flowing granular detergent formulations. Thus, reduction of builders in a formulation, whilst leaving it in the form of free flowing particles, is not straightforward.

Extrusion of detergent compositions is known. Typically, these compositions comprise solid structurants in the extruded mass. Usually the references do not envisage any coating of the extruded particles. When coating is mentioned it generally takes the form of a dusting of fine particulate matter to improve flow or reduce stickiness.
WO9932599 describes a method of manufacturing laundry detergent particles, being an extrusion method in which a builder and surfactant, the latter comprising as a major component a sulphated or sulphonated anionic surfactant, are fed into an extruder, mechanically worked at a temperature of at least 40 °C, preferably at least 60 °C, and extruded through an extrusion head having a multiplicity of extrusion apertures. In most examples, the surfactant is fed to the extruder along with builder in a weight ratio of more than 1 part builder to 2 parts surfactant. In Example 6, PAS paste was dried and extruded. Such PAS noodles are well known in the prior art. The noodles are typically cylindrical in shape and their length exceeds their diameter, as described in example 2. The noodles may be spheronised and are said to be useful as intermediates, to be used by formulators of laundry powders, in producing washing powders of high density. No coating is suggested.

US 5955418 discloses a process in which Sulphate surfactants (possibly blended with other surfactants) may be extruded along with builder material, such as layered silicate. After spheronisation the sticky granules are coated by spraying on nonionic and then dusting with an inorganic powder, such as zeolite or powdered silica. Bhighteners or perfume may be added to the nonionic.

DE 19622443 describes a similar coating of an extruded particle. Once again, the extruded particle contains structuring solids and the coating is a nonionic and optical bhightener mix.

JP1 13 10790A2 describes a process in which a detergent composition comprising surfactant and silicate may be extruded and formed into small diameter granules. After extrusion the material is further granulated and is dusted with fine non-deliquescent material, such as zeolite; alkaline earth silicate; alkaline earth carbonate; alkaline earth sulphate, such as calcium sulphate and magnesium
carbonate; sodium or potassium sulphate. The fine material may be applied as dispersions or solutions in water.

US5152932 discloses the possible extrusion of a molten surfactant paste composition to form particles. The examples do not employ this process variant. The particles are not coated.

Coating of detergent particles to improve their appearance is described in US7022660. Coatings are said to make brighter whiter particles and to reduce stickiness. Non-hydratable inorganic double salt (e.g. Burkeite) coatings are preferred and agglomerated particles of standard size are preferred. The mechanism for achieving the desired smooth coating is suggested to be the smoothing of irregularities and the filling of crevices on the surface of the particles. No data are given to confirm the smoothness of the coating. The application of the coating is claimed to reduce the surface area of the particle, but it is not measured.

**Summary of the Invention**

According to the present invention there is provided a high active detergent particle with Ra less than 6 µm obtainable by extruding surfactant blends with less than 5 wt%, inorganic structurant to make a hard extruded particle and spray coating the particle with an inorganic salt from aqueous solution to form a coating comprising 3 to 40 wt% of the inorganic salt.

Preferably, the uncoated extruded particles contain no inorganic structurants such as silicate, zeolite. Such solid particulate inclusions lead to a roughening of the surface of the extruded particle and make cutting the extrudates more difficult. This may lead to loss of coating smoothness and a greater distribution of particle sizes among the cut and coated particles.
The coating is preferably coloured and the colour of the extruded particle is most preferably changed by application of the coating. The high active detergent particle may contain perfume in the particle.

Use of sodium carbonate as a coating leads to softening of the water before the surfactant is released. This is especially useful in very hard water areas where even normally calcium tolerant surfactant blends can experience some loss of detergency performance due to extreme water hardness.

The high active detergent particle may take the shape of an oblate spheroid. The diameter of the particle may be greater than 2 mm, preferably greater than 3 mm, most preferably greater than 4 mm.

The coated high active detergent particle is preferably made using a process comprising the steps of:

a) feeding a surfactant blend to an extruder and extruding it to form an extrudate with a diameter of at least 3 mm, preferably at least 4 mm,

b) cutting the extruded material so that the particles formed have a thickness less than their diameter and greater than 0.2 mm,

c) coating the cut particles by applying 5 to 40 wt% of a soluble salt by spraying on an aqueous solution of the salt and drying it.

In one preferred embodiment the high active detergent particle is suitably made using a process comprising the steps of:

a) forming a liquid surfactant blend comprising a major amount of surfactant and a minor amount of water, the surfactant part consisting of at least 51 wt% linear
alkylbenzene sulfonate and at least one co-surfactant, the surfactant blend consisting of at most 20 wt% nonionic surfactant;

b) drying the liquid surfactant blend of step (a) in an evaporator or drier to a moisture content of at most 1.5 wt% and cooling the output from the evaporator or dryer;

c) feeding the cooled material, which output comprises at least 93 wt% surfactant blend with a major part of LAS, to an extruder, optionally along with less than 10 wt% of other materials such as perfume, fluoresces and extruding the surfactant blend to form an extrudate while periodically cutting the extrudate to form hard detergent particles with a diameter across the extruder of greater than 2 mm and a thickness along the axis of the extruder of greater than 0.2 mm, provided that the diameter is greater than the thickness;

d) coating the extruded hard detergent particles with up to 30 wt% inorganic coating material.

The blend in step (a) preferably comprises at least 60 wt% total surfactant and at most 40 wt% water.

The blend made in step (b) may be calcium tolerant according to the test hereinbefore described.

Optionally, to reduce the size of the input to the extruder, the cooled output from the evaporator or drier stage (b) comprising at least 95 wt% preferably 96 wt%, more preferably 97 wt%, most preferably 98 wt% surfactant is transferred to a mill and milled to particles of less than 1.5 mm, preferably less than 1 mm before it is fed to the extrusion step (c). A powdered flow aid such as Aerosil®, Alusil®, or Microsil®; with a particle diameter of from 0.1 to 10 µm may be added to the mill
in an amount of 0.5 to 5 wt%, preferably 0.5 to 3 wt% (based on output from the mill) and blended into the particles during milling.

The temperature of the blend desirably does not exceed 45 °C, and preferably does not exceed 40°C, during the extrusion step (c).

Perfume may be added to the extruder.

Advantageously, the surfactant blend is dried in step (b) to a moisture content of less than 1.2 wt%, and most preferably less than 1 wt%.

The evaporator or drier is preferably a wiped film evaporator or a Chemithon® turbo-tube type drier.

The invention also comprises a detergent composition comprising a major part of the high active detergent particles. Preferably, it comprises at least 70 wt%, more preferably at least 85 wt% of the detergent particles. The detergent composition may further comprise at least 2 wt% antifoam particles to reduce foaming, especially when used in a front loading automatic washing machine.

Compositions with up to 100 wt% of the low Ra particles are possible when basic additives are incorporated into the extruded particles, or into their coating.

Preferably, the co-surfactant in the surfactant blend is chosen from the group consisting of: SLES, and nonionic, together with optional soap and mixtures thereof. The only proviso is that when nonionic is used the upper limit for the amount of nonionic surfactant has been found to be 20 wt% of the total surfactant to avoid the dried material being too soft and cohesive to extrude because it has a hardness value less than 0.5 MPa.
The output from step b, or the intermediate milling step, if used, is fed to an extruder, optionally along with minor amounts (less than 10wt%, preferably less than 5 wt% total) of other materials such as perfume and/or fluorescer, and the mixture of materials fed to the extruder is extruded to form an extrudate with a diameter of greater than 2 mm, preferably greater than 3 mm, more preferably greater than 4 mm and preferably with a diameter of less than 7 mm, most preferably less than 5 mm, while periodically cutting the extrudate to form hard detergent particles with a maximum thickness of greater than 0.2 mm and less than 3 mm, preferably less than 2 mm, most preferably less than about 1.5 mm and more than about 0.5 mm, even 0.7 mm. Whilst the preferred extrudate is of circular cross section, the invention also encompasses other cross sections such as triangular, rectangular and even complex cross sections, such as one mimicking a flower with rotationally symmetrical "petals". Indeed the invention can be operated on any extrudate that can be forced through a hole in the extruder or extruder plate; the key being that the average thickness of the extrudate should be kept below the level where dissolution will be slow. As discussed above this is a thickness of about 2 mm. Desirably multiple extrusions are made simultaneously and they may all have the same cross section or may have different cross sections. Normally they will all have the same length as they are cut off by the knife. The cutting knife should be as thin as possible to allow high speed extrusion and minimal distortion of the extrudate during cutting. The only major constraint that we have found for the surfactant blend extrusion is that the extrusion should take place at a temperature of less than 45°C, preferably less than 40°C to avoid stickiness and facilitate cutting. The other major point to note is that the extrudates according to the present process are cut so that their major dimension is across the extruder and the minor dimension is along the axis of the extruder. This is the opposite to the normal extrusion of surfactants. Cutting in this way increases the surface area that is a "cut" surface. It also allows the extruded particle to expand considerably along its axis after cutting, whilst maintaining a relatively high surface to volume ratio, which is believed to increase
its solubility and also results in an attractive biconvex, or lentil, appearance. Elsewhere we refer to this shape as an oblate spheroid. This is essentially a rotation of an ellipse about its minor axis.

It is surprising that at very low water contents the LAS containing surfactant blends can be extruded to make solid detergent particles that are hard enough to be used without any need to be structured by inorganic materials or other structurants as commonly found in prior art extruded detergent particles. Thus, the amount of surfactant in the detergent particle can be much higher and the amount of builder in the detergent particle can be much lower.

The extruded hard detergent particles may be coated by transferring them to a fluid bed and spraying onto them up to 30 wt% (based on coated detergent particle) of powdered inorganic material in aqueous solution and drying off the water.

If the coating material is not contributing to the wash performance of the composition then it is desirable to keep the level of coating as low as possible, preferably less than 20wt%, more preferably less than 15wt% or even 10wt% or as low as 5wt%, especially for larger extruded particles with a surface area to volume ratio of greater than 4 mm⁻¹.

Surprisingly we have found that at low coating levels the appearance of the coating is very pleasing. Without wishing to be bound by theory, we believe that this high quality coating appearance is due to the smoothness of the underlying extruded and cut particle. By starting with a smooth surface, we unexpectedly found it easy to obtain a high quality coating finish (as measured by light reflectance and smoothness) using simple coating techniques.
It is preferred that the coating is coloured. Particles of different colours may be used in admixture, or they can be blended with contrasting powder. Of course, particles of the same colour as one another may also be used to form a full composition. As described above the coating quality and appearance is very good due to the excellent surface of the cut extrudates onto which the coating is applied in association with the large particle size and SA/ ratios of the preferred particles.

It is particularly preferred that the detergent particles comprise perfume. The perfume may be added into the extruder or premixed with the surfactant blend in the mill, or in a mixer placed after the mill, either as a liquid or as encapsulated perfume particles. In an alternative process, the perfume may be mixed with a nonionic material and blended. Perfume may also be introduced into the composition by means of a separate perfume granule and then the detergent particle does not need to comprise any perfume.

Detailed description of the invention

The Surfactant Blend

Surfactant blends that do not require builders to be present for effective detergency in hard water are preferred. Such blends are called calcium tolerant surfactant blends if they pass the test set out hereinafter. However, the invention may also be of use for washing with soft water, either naturally occurring or made using a water softener. In this case, calcium tolerance is no longer important and blends other than calcium tolerant ones may be used.

Calcium-tolerance of the surfactant blend is tested as follows:

The surfactant blend in question is prepared at a concentration of 0.7 g surfactant solids per litre of water containing sufficient calcium ions to give a French
hardness of 40 (4 x 10^{-3} \text{ Molar Ca}^{2+})$. Other hardness ion free electrolytes such as sodium chloride, sodium sulphate, and sodium hydroxide are added to the solution to adjust the ionic strength to 0.05M and the pH to 10. The adsorption of light of wavelength 540 nm through 4 mm of sample is measured 15 minutes after sample preparation. Ten measurements are made and an average value is calculated. Samples that give an absorption value of less than 0.08 are deemed to be calcium tolerant.

Examples of surfactant blends that satisfy the above test for calcium tolerance include those having a major part of LAS surfactant (which is not of itself calcium tolerant) blended with one or more other surfactants (co-surfactants) that are calcium tolerant to give a blend that is sufficiently calcium tolerant to be usable with little or no builder and to pass the given test. Suitable calcium tolerant co-surfactants include SLES 1-7EO, and alkyl ethoxylate non-ionic surfactants, particularly those with melting points less than 40°C. In a further refinement of the surfactant system it has been found that calcium tolerant LAS systems formed by the addition of SLES or High chain-length nonionic often require use of a third surfactant to more closely match the cleaning performance of fully built detergent systems. Suitable third surfactants include betaines, amine oxides, and cationics, such as the Praepagen® materials from Clariant.

A LAS SLES surfactant blend has a superior foam profile to a LAS Nonionic surfactant blend and is therefore preferred for hand washing formulations requiring high levels of foam. SLES may be used at levels of up to 30%.

Addition of a nonionic surfactant (5-20%) to LAS changes the behaviour of the surfactant blend in the dryer. This gives a surprising increase in throughput. Nonionic 7EO may be used at levels of between 5 and 20% based on dry surfactant. NI 30EO may be used at levels of up to 20%.
Material Characteristics of the Surfactant Blends

To enable sufficient Calcium tolerance for LAS blends an additional surfactant material such as SLES or Nonionic surfactant is added. The level that needs to be added to achieve calcium tolerance for the LAS rich blend varies according to the exact surfactant system but the effect can easily be tested to arrive at a suitable level for calcium tolerance. The added non-LAS surfactants should also be liquid-like and not exceed 50wt% of the total surfactant, the balance of surfactant being LAS. Preferred added surfactants are selected from Nonionic 7EO and/or Nonionic 30EO and/or SLES and/or PAS.

The structuring of the surfactant blend is done by the LAS. This eliminates the need for the usual inorganic structurant, such as silicate. However, such an approach is found to require the surfactant blend to be dried to very low moisture contents of at most 2 wt%, preferably at most 1.5 wt% and most preferably at most 1 wt%. At these moisture levels, a high active mixed surfactant detergent particle with dimensional integrity and free flowing behaviour can be extruded.

Increasing the nonionic content within the LAS rich surfactant blend reduces the hardness of the dried blend. Hardness is also related to moisture content of the dried blend. The maximum nonionic level that can be included is about 20%, above this the dried blend is too soft to mill before the extruder, or cut after the extruder. The minimum inclusion level of nonionic in a LAS/nonionic binary blend is about 5%.

A preferred detergent composition has a LAS/SLES surfactant blend. However, the replacement of 20% of the LAS with PAS results in a product with improved storage stability and a similar cleaning profile.
Processing

Blending
The surfactants are mixed together before being input to the drier. Conventional mixing equipment is used.

Drying
To achieve the very low moisture content of the surfactant blend, scraped film devices may be used. A preferred form of scraped film device is a wiped film evaporator. One such suitable wiped film evaporator is the "Dryex system" based on a wiped film evaporator available from Ballestra S.p.A.. Alternative drying equipment includes tube-type driers, such as a Chemithon® drier, and soap driers.

Chilling and milling
The hot material exiting the scraped film drier is subsequently cooled and broken up into suitable sized pieces to feed to the extruder. Simultaneous cooling and breaking into flakes may conveniently be carried out using a chill roll. If the flakes from the chill roll are not suitable for direct feed to the extruder then they can be milled in a milling apparatus and/or they can be blended with other liquid or solid ingredients in a blending and milling apparatus, such as a ribbon mill. Such milled or blended material is desirably of particle size 1 mm or less for feeding to the extruder.

It is particularly advantageous to add a milling aid at this point in the process. Particulate material with a mean particle size of 10 nm to 10 µm may be used as a milling aid. Among such materials, there may be mentioned, by way of example: aerosil®, alusil®, and microsil®.
Extruding and cutting
The extruder provides further opportunities to blend in ingredients other than surfactants, or even to add further surfactants. However, it is generally preferred that all of the anionic surfactant, or other surfactant supplied in admixture with water; i.e. as paste or as solution, is added into the drier to ensure that the water content can then be reduced and the material fed to and through the extruder is sufficiently dry. Additional materials that can be blended into the extruder are thus mainly those that are used at very low levels in a detergent composition: such as fluorescences shading dye, enzymes, perfume, silicone antifoams, polymeric additives and preservatives. The limit on such additional materials blended in the extruder has been found to be about 10wt% but it is preferred to keep them at or below 5 wt%. Solid additives are generally preferred. Liquids, such as perfume may be added at levels up to 2.5 wt%, preferably up to 1.5 wt%.

The output from the extruder is shaped by the die plate used. The extruded material has a tendency to swell up in the centre relative to the periphery. We have found that if a cylindrical extrudate is regularly sliced as it exits the extruder the resulting shapes are short cylinders with two convex ends. These particles may be described as oblate spheroids. This shape is pleasing visually and its slightly rounded appearance also contributes to improved flow properties of the extruded particles in bulk.

The sliced output from the extruder can be sent directly to the coating stage or it may be stored until needed.

Coating
The sliced extruded particles are coated. This allows the particles to be coloured easily and generally improves their appearance. It also further reduces the stickiness to a point where the particles are free flowing. In this coated state, they
can be used without any need for separation by base powder or other solid diluents.

By coating such large extruded particles the thickness of coating obtainable by use of a coating level of say 5 wt% is much greater than would be achieved on typically sized detergent granules (0.5-2mm diameter sphere).

The extruded particles can be considered as oblate spheroids with a major radius "a" and minor radius "b". Hence, the surface area(S) to volume (V) ratio can be calculated as:

\[
\frac{S}{V} = \frac{3}{2b} + \frac{3b}{4a^2} \ln \left( \frac{1+\varepsilon}{1-\varepsilon} \right) \text{mm}^{-1}
\]

When \(\varepsilon\) is the eccentricity of the particle.

For optimum dissolution properties, this surface area to volume ratio must be greater than 3 mm\(^{-1}\). However, the coating thickness is inversely proportional to this coefficient and hence for the coating the ratio "Surface area of coated particle" divided by "Volume of coated particle" should be less than 15 mm\(^{-1}\).

By using the process of the invention, a more effective coating can be obtained at a lower level of coating material. Use of a coating deposited by crystallisation from an aqueous solution appears to give advantageous dissolution benefits and the coating gives a good colour to the detergent particle, even at low deposition levels. An aqueous spray-on of the coating solution in a fluidised bed has been found to give good results and may also generate a slight rounding of the detergent particles during the fluidisation process.
Suitable coating solutions include sodium carbonate, possibly in admixture with sodium sulphate, and sodium chloride. Food dyes, shading dyes, fluorescer and other optical modifiers can be added to the coating by dissolving them in the spray-on solution or dispersion. Use of a builder salt such as sodium carbonate is particularly advantageous because it allows the detergent particle to have an even better performance by buffering the system in use at an ideal pH for maximum detergency of the anionic surfactant system. It also increases ionic strength, which is known to improve cleaning in hard water, and it is compatible with other detergent ingredients that may be admixed with the coated extruded detergent particles. If a fluid bed is used to apply the coating solution, the skilled worker will know how to adjust the spray conditions in terms of Stokes number and possibly Akkermans number (FNm) so that the particles are coated and not significantly agglomerated. Suitable teaching to assist in this may be found in EP1 187903, EP993505 and Powder technology 65 (1991) 257-272 (Ennis).

It will be appreciated by those skilled in the art that multiple layered coatings, of the same or different coating materials, could be applied, but a single coating layer is preferred, for simplicity of operation, and to maximise the thickness of the coating. The amount of coating should lay in the range 3 to 40 wt% of the particle, preferably 10, or even 20 to 40 wt% for the best results in terms of anti-caking properties of the detergent particles.

The extruded particulate detergent composition
The particles dissolve easily in water and leave very low or no residues on dissolution, due to the absence of insoluble structurant materials, such as zeolite. The coated particles have an exceptional visual appearance, due to the smoothness of the coating coupled with the smoothness of the underlying particles, which is also believed to be a result of the lack of particulate structuring material in the extruded particles.
The invention will now be further described by way of example only.

In the examples, the following nomenclature is used:

- **LAS** - means neutralised LAS acid (LABSA)
- **LAB** - means the "linear" alkylate
- **LABSA** - means LAS acid.
- **PAS** - means primary alkyl sulphate
- **SCMC** - Sodium carboxymethyl cellulose
- **SLES (XEO)** - means sodium lauryl ether sulphate
  (X moles average ethoxylation)

Test parameters used in the examples are defined and determined in accordance with the following:

**Unconfined Compression Test (UCT)**

In this test, freshly produced detergent composition was compressed into a compact and the force required to break the compact was measured. The detergent composition was loaded into a cylinder and the surface levelled. A 50 g plastic disc was placed on top of the detergent composition and a 10 kg weighted plunger was placed slowly on top of the disc and allowed to remain in position for 2 minutes. The weight and plunger were then removed and the cylinder removed carefully from the detergent composition to leave a free-standing cylinder of detergent composition with the 50g plastic disc on top of it. If the compact were unbroken, a second 50 g plastic disc was placed on top of the first and left for approximately ten seconds. Then if the compact were still unbroken, a 100 g disc was added to the plastic discs and left for ten seconds. Then the weight was increased in 250g increments at 10 second intervals until the compact collapsed.

The total weight needed to effect collapse was noted.
For freshly made detergent composition tested under ambient temperature conditions, the cohesiveness of the detergent composition was classified by the weight \( (w) \) as follows, (assuming the standard 10.0 kg compaction load is used).

\[
\begin{align*}
5 & \quad w < 1 \text{ kg} \quad \text{Good flowing.} \\
1 \text{ kg} < w < 2 \text{ kg} & \quad \text{Moderate flowing.} \\
2 \text{ kg} < w < 5 \text{ kg} & \quad \text{Cohesive.} \\
5 \text{ kg} < w & \quad \text{Very cohesive.}
\end{align*}
\]

**Dynamic Flow Rate (DFR)**

Dynamic Flow Rate (DFR) in \( \text{ml/sec} \) was measured using a cylindrical glass tube having an internal diameter of 35 mm and a length of 600 mm. The tube was securely clamped with its longitudinal axis vertical. Its lower end was terminated by means of a smooth cone of polyvinyl chloride having an internal angle of 15 DEG and a lower outlet orifice of diameter 22.5 mm. A beam sensor was positioned 150 mm above the outlet, and a second beam sensor was positioned 250 mm above the first sensor.

To determine the dynamic flow rate of a detergent composition sample, the outlet orifice was temporarily closed, for example, by covering with a piece of card, and detergent composition was poured into the top of the cylinder until the detergent composition level was about 100 mm above the upper sensor. The outlet was then opened and the time \( t \) (seconds) taken for the detergent composition level to fall from the upper sensor to the lower sensor was measured electronically. The DFR is the tube volume between the sensors, divided by the time measured.

**Bulk Density (BD)**

"Bulk density" means the bulk density of the whole detergent composition in the uncompacted (untapped) aerated form. It was measured by taking the increase in weight due to filling a 1 litre container with the detergent composition.
Equilibrium Relative Humidity (ERH)

Water activity (usually given the parameter Aw) is related to equilibrium relative humidity (%ERH) by the equation:

\[ \text{ERH} = 100 \times \text{Aw} \]

5

Aw = equilibrium partial pressure of moisture/saturation partial pressure of moisture at that temp.

A value for water activity of 1 (ERH=100) indicates pure water, whereas zero indicates total absence of water.

Example 1

Surfactant raw materials were mixed together to give a 67wt% active paste comprising 56.5 parts LAS, 15.2 parts PAS and 28.3 parts SLES.

Raw Materials used were:

- LABSA
- Caustic (48% Solution)
- PAS
- SLES(3E0) Stepan BES70

The paste was pre-heated to the feed temperature and fed to the top of a wiped film evaporator to reduce the moisture content and produce a solid intimate surfactant blend, which passed the calcium tolerance test. The conditions used to produce this LAS/PAS/SLES blend are given in Table 1.
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Table 1

<table>
<thead>
<tr>
<th>Feed</th>
<th>Jacket Vessel Temp.</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Nominal Throughput</td>
<td>65 kg/hr</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>1.2 kg/l</td>
</tr>
<tr>
<td>Product</td>
<td>Moisture(KF*)</td>
<td>1.0 %</td>
</tr>
<tr>
<td></td>
<td>Free NaOH</td>
<td>0.16 %</td>
</tr>
</tbody>
</table>

*analysed by Karl Fischer method

On exit from the base of the wiped film evaporator, the dried surfactant blend dropped onto a chill roll, where it was cooled to less than 30°C.

After leaving the chill roll, the cooled dried surfactant blend particles were milled using a hammer mill, 2% Aerosil® was also added to the hammer mill as a mill aid. The resulting milled material is hygroscopic and so it was stored in sealed containers. Its properties are given in table 2.

Table 2

<table>
<thead>
<tr>
<th>ERH</th>
<th>Phys Props</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UCT (kg)</td>
<td>DFR (ml/s)</td>
</tr>
<tr>
<td>8.7</td>
<td>1.9</td>
<td>70/71</td>
</tr>
</tbody>
</table>

The cooled dried milled composition was fed to a twin-screw co-rotating extruder fitted with a shaped orifice plate and cutter blade.

The average particle diameter and thickness of samples of the extruded particles were found to be 4.46 mm and 1.13 mm respectively. The standard deviation was acceptably low.

The particles were then coated using a Strea 1 fluid bed. The coating was added as an aqueous solution and coating completed under conditions given in Table 3.

Coating wt% is based on weight of the coated particle.
As can be seen from Table 3 the samples have different coating levels. These samples and additional samples made using the same process were then equilibrated at 48 and 65% relative humidity and their hardness measured. The hardness measurements are shown in Table 4.
Table 4

<table>
<thead>
<tr>
<th>Coating Level</th>
<th>Average @ 20°C / 48%RH (%)</th>
<th>Average @ 21°C / 65%RH (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>15</td>
<td>0.40</td>
<td>0.22</td>
</tr>
<tr>
<td>25</td>
<td>0.85</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Example 2

A mixture of LAB ex Huntsman, nonionic and PEG in the ratio 100:1:0:2 was sulphonated at pilot plant scale to convert the LAB to LABSA and then neutralised with caustic solution to make the LABSA into LAS.

The only moisture added to the system was contained in the 50% sodium hydroxide solution (low chloride) used as the neutralisation agent. Details of the materials are as specified in table 5. The neutralisation reaction on the LABSA, (Linear Alkyl Benzene Sulphonic acid) was completed in the presence of nonionic and PEG. An 85w% active paste comprising anionic surfactant, nonionic and PEG that could be pumped with a vane pump was produced. The neutralisation process was continued for 8 hours.
The paste surfactant mixture was dried in a Turbo-Tube Dryer and milled using a hammer mill: no mill aid was added. The properties of the resulting dried milled composition are given in Table 6.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Supplier/Trade name</th>
<th>% Active</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 4000</td>
<td>BP Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>Linear Alkyl Benzene,(LAB)</td>
<td>Huntsman/ A225</td>
<td>98-100</td>
</tr>
<tr>
<td>Nonionic 7EO</td>
<td>Shell Chemicals / Neodol 25-7</td>
<td>100</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>Univar</td>
<td>50</td>
</tr>
</tbody>
</table>

T90 = time in seconds for change in the water conductivity to reach 90% of its final magnitude when a 250 mg sample is placed into 500 ml of stirred demineralised water at 25 °C.

The dried and milled composition was fed to a twin screw extruder and extruded. The average maximum thickness of the extruded particles was 1.13 mm (sd 0.18) and their average particle diameter was 4.46 mm (sd 0.26).
The uncoated extruded particles were coated using a coating level of 15 wt%. This was achieved by spraying a 25 wt% sodium carbonate solution, containing 0.5wt% orange dye, into a fluid bed and evaporating off the excess moisture. The high active extruded particles being coated are hygroscopic and temperature sensitive. Thus, at all times a balance was maintained between the spray rate and evaporation rate of the solution and the temperature of the bed. The fluidised bed is operated as known to the skilled worker in order to avoid agglomeration of the material. The coating conditions used are given in table 7.

Table 7

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Result</th>
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<tr>
<td>Solid Mass</td>
<td>1.5kg</td>
</tr>
<tr>
<td>Air Inlet Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Air Outlet temperature</td>
<td>35°C</td>
</tr>
<tr>
<td>Spray Rate</td>
<td>22 g/min</td>
</tr>
<tr>
<td>Spray Temperature</td>
<td>40°C</td>
</tr>
</tbody>
</table>

Example 3

100 parts of the milled material produced in example 1 at the exit of the mill was mixed in a tumbling mixer with 1.15 parts fluorescer and 3 parts SCMC. This mixture was then fed to a twin-screw co-rotating extruder along with 1.15 parts perfume liquid. The resulting mixture was extruded through a shaped orifice plate and cut with a cutter blade to produce detergent particles comprising just under 4 wt% perfume, fluorescer and SCMC in addition to surfactant.

The extruded particles were determined to have an average thickness of 1.11 mm (sd 0.18) range 0.9 to 1.4. The T90 dissolution time was 73 seconds.

Caking on extended storage was acceptable after coating with 25 wt% sodium carbonate. The material was sealed in conventional un laminated cardboard packs and stored at 28°C and 70% relative humidity for 8 weeks. Packs were examined during this period for acceptable powder flow properties/caking by
pouring the product from the pack onto a tray and visually estimating the percentage of lumped powder. Results are given in Table 8.

<table>
<thead>
<tr>
<th>Pack Sample</th>
<th>Flow</th>
<th>Residue in Pack</th>
<th>Lumps ex pack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>Satisfactory</td>
<td>25-50%</td>
<td>25%</td>
</tr>
<tr>
<td>Uncoated</td>
<td>No flow</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Example 4

These examples show that the superior appearance of the extruded particles is due to the uncoated extruded particle being smoother than conventional agglomerated detergent particles and that the final coated surface is smoother still. This need for the underlying surface to be smooth before a coating is applied is known generally but it was nevertheless surprising just how improved the coated particles appear compared with other conventional detergent particles. The underlying smoothness of the extruded particles is thought to be assisted by their not containing solid structuring materials, unlike prior art extruded particles. The particles are also superior in appearance when compared to prior art granules made by other processes, especially agglomerated granules.

In order to determine the value of Ra (average surface roughness) for each particle sample we used a non-contact optical profilometer equipment comprising a low powered near-infrared Laser Stylus mounted on a moveable stage controlled by a computer. A Laser stylus is a displacement transducer based on technology found in a compact disc player. In a compact disc player, a focussed laser is used to record the pits embedded within the disk. Since the disk wobbles slightly as it spins, an auto-focus mechanism is needed to maintain the in-focus condition. This auto-focus mechanism uses the light reflected from the disc to generate an error signal that can be used to lock the laser onto the surface. The error signal is minimised
through the real-time adjustment of a lens position, and a feedback loop to achieve an acceptable response time.

To use such a device to measure surface topography requires the laser to be focussed on the surface, and then the surface moved in a raster fashion (line scan Y and step scan X) underneath it. A recording of the lens position gives a measurement of the surface height variation.

The major component of the Laser Profilometer is a laser displacement transducer (Rodenstock Laser Stylus RM 600 LS1 0) which operates in the near-infrared at 780 nm. This transducer gives a spot size of about 1.3 µm on the measured surface, has a distance resolution of 1 nm and an operational range of ±400 µm. The 'stand-off' distance between the end of the transducer and the measured surface is about 10 mm, in air, and the full included cone angle of the focused beam is approximately 47°. This transducer is an example of an Optical follower' that utilises auto-focusing optics to 'lock-onto' an interface and to measure its location relative to a reference position internal to the device.

Ra (average surface roughness) is one of the most effective surface roughness measures and is commonly adopted in general engineering practice. It gives a good general description of the height variations in the surface. A mean line is first found that is parallel to the general surface direction and divides the surface in such a way that the sum of the areas formed above the line is equal to the sum of the areas formed below the line. The surface roughness Ra is now given by the sum of the absolute values of all the areas above and below the mean line divided by the sampling length.

The test sample is mounted on the stage to reflect the laser. The sample is held sufficiently firmly to prevent any spurious movement during scanning.
Data is evaluated on a computer where programs flatten the topography, line by line, to leave deviations net of tilt and curvature. Ra is the mean roughness of the measured surface heights of a sample.

Because some of the original sample particles proved to be insufficiently reflective for the profilometer instrument to be able to lock onto the surface, we made surface replicates of all three test particles using a material called Silflo (Ex-Flexico), which is a light-bodies silicone rubber impression material that readily flows into surface features. The material was prepared and then a coated particle was pushed (gently) into the rubber before it hardened. On removing the particle, a surface replicate is left in the Silflo.

We then placed this replicate impression into the laser profilometer and measured a section, up to 1000 µm by 1000 µm, with data taken every µm in both x and y directions. For each type of particle, we measured multiple replicates in this way. Averaged Results are given in Table 9. The details of the original particles are given below.

Extruded particles were made according to the first part of the process of example 1 and using a blend of LAS/PAS/SLES with ratio 58.3/14.6/27. The extruded particles had a circular cross section and dimensions of about 5 mm diameter by 1 mm.

For example 4.1 a fraction of these extruded particles was coated using a 25% sodium carbonate coating solution to give a final coating level of 30 wt%. For examples 4.2 we used a slightly lower coating level and for example 4.3 we used a Burkeite double salt as the sprayed on inorganic salt coating material.

The conventional High active granule used in comparative examples A, B and C
was made using the process described in WO2002/24853 and had the composition:

<p>| | |</p>
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<tr>
<td>LAS</td>
<td>65.5%</td>
</tr>
<tr>
<td>Soda Ash</td>
<td>11.5%</td>
</tr>
<tr>
<td>Zeolite</td>
<td>17.9%</td>
</tr>
<tr>
<td>Sodium Sulphate</td>
<td>2.2%</td>
</tr>
<tr>
<td>Water and minors</td>
<td>balance</td>
</tr>
</tbody>
</table>

To be as good a comparison as possible with the larger extruded particles we used an oversized granule in Example A. (retained on a 1.18mm sieve). Even so, due to this being smaller than the extruded particles, we could only measure a 500µm by 500µm segment.

A sprayed on Burkeite coating at the same level as example 4.3 was used for comparative example C.

<table>
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<tr>
<th>Ex</th>
<th>Ra (µm) (ave)</th>
</tr>
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<tr>
<td>A</td>
<td>19.9</td>
</tr>
<tr>
<td>B</td>
<td>11.3</td>
</tr>
<tr>
<td>C</td>
<td>7.6</td>
</tr>
<tr>
<td>D</td>
<td>6.8</td>
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<td>5.9</td>
</tr>
<tr>
<td>4.3</td>
<td>3.2</td>
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Table 9
It can be seen from table 9 that a conventional agglomerated high active granule detergent particle is much rougher than the uncoated extruded particle D. The uncoated oversized agglomerated material A being slightly rougher than the uncoated conventional sized agglomerate B. Even when coated as in comparative example C the agglomerated material, whilst smoother than its uncoated starting material, is nevertheless still comparatively rough and is actually still rougher than the uncoated extruded structurant free example D. When the large diameter extruded material is coated the resulting particles, particle free and that when coated the extruded particle is smoother still. Ra (µm) of less than 6, even less than 4, was achieved for the coated extruded particles. The combination of larger radius of curvature, smooth base particle and coating gives the coated extruded particle a stunning appearance when compared to the typical appearance of a detergent particle. When coupled with a low particle size distribution this leads to a dramatically visually different and enticing particle that consumers would really appreciate is different from their normal product.
Claims

1. A high active detergent particle with Ra less than 6 µm obtainable by extruding surfactant blends with less than 5 wt%, inorganic structurant, to make a hard extruded particle and spray coating the particle with 3 to 40 wt% of soluble inorganic salt.

2. A high active detergent particle according to claim 1 in which the coating is coloured and the colour of the extruded particle is changed by application of the coating.

3. A high active detergent particle according to any preceding claim, which contains perfume in the particle.

4. A high active detergent particle according to any preceding claim, which is an oblate spheroid.

5. A high active detergent particle according to any preceding claim in which the diameter of the extruded particle is greater than 2 mm, preferably greater than 3 mm, most preferably greater than 4 mm.

6. A high active detergent particle according to any preceding claim made using a process comprising the steps of:

   a) feeding a surfactant blend to an extruder and extruding it to form an extrudate with a diameter of at least 3 mm, preferably at least 4 mm,

   b) cutting the extruded material so that the particles formed have a thickness less than their diameter and greater than 0.2 mm,
c) coating the cut particles by applying 5 to 40 wt% of a soluble salt by spraying on an aqueous solution of the salt and drying it.

7. A high active detergent particle according to claim 6 made using a process in which the blend fed to the extruder comprises at least 80 wt%, preferably at least 90 wt%, more preferably at least 95 wt%, total surfactant.

8. A high active detergent particle according to claim 6 or claim 7 made using a process in which the surfactant blend fed to the extruder is calcium tolerant according to the test hereinbefore described.

9. A high active detergent particle according to any one of claims 6 to 8 made using a process in which perfume is added to the extruder.

10. A high active detergent particle according to any one of claims 6 to 9 made using a process comprising the steps of:

a) forming a liquid surfactant blend comprising a major amount of surfactant and a minor amount of water, the surfactant part consisting of at least 51 wt% linear alkylbenzene sulfonate and at least one co-surfactant, the surfactant blend consisting of at most 20 wt% nonionic surfactant;

b) drying the liquid surfactant blend of step (a) in an evaporator or drier to a moisture content of at most 1.5 wt% and cooling the output from the evaporator or dryer;

c) feeding the cooled material, which output comprises at least 93 wt% surfactant blend with a major part of LAS, to an extruder, optionally along with less than 10 wt% of other materials such as perfume, fluorescer, and extruding the surfactant
blend to form an extrudate while periodically cutting the extrudate to form hard
detergent particles with a diameter across the extruder of greater than
2 mm and a thickness along the axis of the extruder of greater than 0.2 mm,
provided that the diameter is greater than the thickness;

\[ d \]

coating the extruded hard detergent particles with up to 30 wt% soluble
inorganic coating material.

11. A detergent composition comprising a major part of the high active detergent
particles of any preceding claim.

12. A detergent composition according to claim 11 comprising at least 70 wt%,
preferably at least 85 wt% of the detergent particles.

13. A detergent composition according to claim 11 or 12 further comprising at
least 2 wt% antifoam particles.
**INTERNATIONAL SEARCH REPORT**

**International application No**

PCT/EP2010/055257

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### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIIID

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

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### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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### Section Notes

- Special categories of cited documents:
  - 'A' document defining the general state of the art which is not considered to be of particular relevance.
  - 'E' earlier document but published on or after the international filing date.
  - 'L' document which may throw doubts on prior art claims or which is cited to establish the publication date of another citation or other special reasons (as specified).
  - '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.

- '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.

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- '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.

- 'S' document member of the same patent family.

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**Date of the actual completion of the international search**

19 May 2010

**Date of mailing of the international search report**

04/06/2010

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**Name and mailing address of the ISA/Authorized officer**

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Culmann, J

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Form PCT/ISA/210 (second sheet) (April 2005)
#### INTERNATIONAL SEARCH REPORT

**C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

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