

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 1 469 061 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
20.10.2004 Bulletin 2004/43

(51) Int Cl.<sup>7</sup>: C11D 17/00

(21) Application number: 04075672.8

(22) Date of filing: 09.03.2004

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IT LI LU MC NL PL PT RO SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK**

(30) Priority: 16.04.2003 EP 03076119

(71) Applicants:  
• **UNILEVER N.V.**  
**3013 AL Rotterdam (NL)**  
Designated Contracting States:  
**AT BE BG CH CZ DE DK EE ES FI FR GR HU IT  
NL PT SE SI SK TR**  
• **UNILEVER PLC**  
**London EC4P 4BQ (GB)**  
Designated Contracting States:  
**IE GB CY**

(72) Inventors:  
• **Nauta, Lammert c/o Unilever R&D Vlaardingen  
3133 AT Vlaardingen (NL)**  
• **Stuut, Iwan c/o Unilever R&D Vlaardingen  
3133 AT Vlaardingen (NL)**

(74) Representative: **Joppe, Hermina L. P. et al  
Unilever N.V.  
Patent Division  
P.O. Box 137  
3130 AC Vlaardingen (NL)**

(54) **Multiphase cleaning tablet comprising a smooth phase and process for the preparation thereof**

(57) A process for the preparation of a multi-phase cleaning tablet comprising a first smooth phase which comprises a meltable material and a second phase, comprising the steps of

- A) treating the outer surface of said smooth phase such that at least part of the outer surface thereof melts;
- B) bringing said melted part of said smooth phase into contact with the outer surface of the second phase such that the melted surface part of the

smooth phase is used as the contact surface; and  
C) pressing the two phases together to ensure adequate adhesion of the first smooth phase to the second phase.

EP 1 469 061 A1

## Description

**[0001]** This invention relates to cleaning compositions in the form of tablets for example, for use in fabric washing or machine dishwashing.

**[0002]** Detergent compositions in tablet form have advantages over powdered products in that they do not require measuring and are thus easier to handle and dispense into the washload.

**[0003]** Tablets of a cleaning composition are generally made by compressing or compacting a quantity of the composition in particulate form.

**[0004]** Tablets comprising two or more separate regions have also been described. For example WO 01/42416 describes the production of multi-phase moulded bodies comprising a combination of core moulded bodies and a particulate premix. WO 00/61717 describes a detergent tablet which is characterised in that at least part of its outer surface is smooth. WO 00/04129 describes a multi-phase detergent tablet comprising a first phase in the form of a shaped body having at least one mould therein and a second phase in the form of a particulate solid compressed within said mould.

**[0005]** It is an object of the present invention to provide a method to produce cleaning tablets comprising a smooth phase, wherein the tablets can be produced at high speed at a relatively low cost.

**[0006]** A further objective of the present invention is to provide a method to produce a smooth tablet or phase thereof wherein the choice of materials and the manufacturing method allows the low cost production of tablets of good performance and of good consistency and texture.

**[0007]** The present invention relates to a cleaning tablet which has a plurality of discrete regions with differing compositions, characterised in that at least one first region of the tablet is a smooth region and at least one second region of the tablet which preferably is a solid region of compacted particulate material.

**[0008]** One method of producing smooth phases which can be used in cleaning tablets is first to produce a large quantity e.g. an extruded strand or a log of the material, followed by partitioning this quantity into smaller quantities for example by cutting.

**[0009]** Another method of producing smooth phases may be manufacture pieces of smooth material for example by shaping or by a so-called casting process, whereby a fluid material is introduced into a mould, the material hardens or solidifies in said mould followed by removal of the smooth phases from the mould.

**[0010]** A problem with the use of separately prepared smooth phases is that these require an assembly process to prepare the multi-phase tablet. Such an assembly process often is complicated and may lead to undesirable cost increases.

**[0011]** WO 00/52127 (Henkel) describes a method of preparing multi-phase moulded detergent articles by

compressing a particulate premix, applying one or more adhesive agents and then applying further active substances in solid, high-viscous or plastic form.

**[0012]** WO 01/60695 (P&G) describes a process of 5 making a multi-phase detergent tablet comprising the contacting of a first and second phase below the melting temperature of an adhesive present in the second phase, followed by adhering the two phases by subjecting the mixture to a temperature above the melting temperature of said adhesive.

**[0013]** In a first aspect the present invention relates to a method for the preparation of a multi-phase cleaning tablet comprising a first smooth phase having a weight of from 3 to 10 grammes and comprising a meltable material and a second phase having a weight of from 15 to 15 40 grammes, said method comprising the steps of

20 A) treating the outer surface of said smooth phase such that at least part of the outer surface thereof melts;

B) bringing said melted part of said smooth phase into contact with the outer surface of the second phase such that the melted surface part of the smooth phase is used as a contact surface; and

25 C) pressing the two phases together to ensure adequate adhesion of the smooth phase to the second phase.

**[0014]** In the method of the invention, said melted part 30 of the smooth phase is preferably used as the contact surface.

In a second aspect, the present invention provides a multi-phase cleaning tablet comprising a first smooth phase having a weight of from 3 to 10 grammes and 35 comprising a meltable material and a second phase having a weight of from 15 to 40 grammes, wherein the first phase has been thermally adhered to the second phase according to the method of the invention.

**[0015]** Surprisingly it has been found that the (partial) 40 melting of the outer surface of the smooth phase followed by adhesion of the smooth phase to a second phase of the tablet, provides a cost effective, convenient method to ensure a good quality assembly of the multi-phase tablet. Especially the method can be carried out 45 at a high throughput rate without the need for separate adhesives applied between the two phases and without the need of fully heating the tablet or the entire smooth phase.

**[0016]** Preferably, multi-phase tablets according to 50 the invention and each of the separate phases thereof are of cylindrical shape wherein the two main surfaces (upper side and bottom side) are substantially flat. Preferably the smooth phases (and other phases of the multi-phase tablet) are flat slices of cleaning material, for 55 example having a diameter of from 1 to 10 cm (preferably 2 to 6 cm) and a height of from 0.1 to 5 cm (preferably 0.3 to 1.5 cm).

**[0017]** A preferred embodiment of the invention re-

lates to a multiphase tablet wherein at least one smooth phase is present and additionally one or more other phases are present. Suitably, these additional phases can be smooth or solid. Particularly suitable additional phases are solid phases composed of compacted particulate solids.

**[0018]** The regions of a multi-phase tablet are preferably separate layers within a tablet. However, a discrete region of a tablet could also have other forms for example one or more core(s) or insert(s). In a preferred embodiment, the first region is a smooth layer and the second region is a layer of compacted particulate material. In a further advantageous embodiment, the first region is a core or insert of smooth material embedded in the second region which is a layer of compacted particulate material.

**[0019]** The multi-phase tablet of the invention comprises the smooth phase being present as a distinctive region having a weight of from 3 to 10 grammes. Preferably, the other phases of the tablet together have a weight of 15 to 40 grammes.

**[0020]** For the purpose of this invention the term smooth phase refers to compositions which are on the one hand solid enough to retain their shape at ambient temperature and on the other hand smooth in appearance. Smooth textures are generally of low or no porosity and have -at normal viewing distance- the appearance of a continuous phase for example as opposed to porous and particulate appearance of a compacted particulate material.

**[0021]** Smooth phases for use in an assembly process in accordance to the invention are preferably pre-prepared. Such pre-preparation will normally involve the shaping and/or division of the material of the smooth phase. Examples of suitable processes to prepare smooth phase are casting, extrusion followed by division into pieces, tabletting etc. For example our non-pre-published case EP 0277267 discloses the preparation of compressed shaped smooth phase, our non-pre-published case EP0278247 discloses the preparation of smooth phases by extrusion and our non pre-published case EP 0279186 discloses suitable methods for the cutting of smooth phases.

**[0022]** Sometimes it is preferable that the smooth phase is transparent or translucent. Preferably, this means that the composition has an optical transmissivity of at least 10%, most preferably 20%, still more preferably 30%, through a path length of 0.5 cm at 25° C. These measurements may be obtained using a Perkin Elmer UV/VIS Spectrometer Lambda 12 or a Brinkman PC801 Colorimeter at a wavelength of 520nm, using water as the 100% standard.

**[0023]** The transparency or translucency of the compositions according to the invention does not preclude the composition being coloured, e.g. by addition of a dye, provided that it does not detract substantially from clarity. Examples of suitable smooth phases are given in our non-prepublished application EP 0256833.

**[0024]** In an advantageous embodiment of the invention the smooth phase comprises from 20-80 wt% of non-soap surfactants (based on the total weight of said smooth phase), more preferred from 25 to 75 wt%, most

5 preferred 30 to 70 wt%. It has been found that the combination of a separate smooth first region and these high surfactant levels provide very good dispersing and cleaning properties to the tablet.

**[0025]** Preferably the non-soap surfactants in the first 10 region comprise a combination of anionic surfactants and non-ionic surfactants in a weight ratio of from 5 : 1 to 1 : 5, more preferred 3 : 1 to 1 : 3, more preferred 2 : 1 to 1 : 2. Further surfactants, for example cationic surfactants may equally be present for example at a level 15 of 0.1 to 10 wt% based on the weight of the smooth part.

**[0026]** The smooth region will also comprise a meltable material. Preferably the smooth region is formulated such that it becomes fluid at elevated temperatures, for example somewhere between 30 and 100°C, more preferably between 35-90°C most preferably 40-60°C. The presence of anionic and/or nonionic surfactants as meltable materials in the smooth phase is especially useful.

**[0027]** Other suitable meltable materials are for example diluent materials.

**[0028]** In addition to the non-soap surfactants the smooth region may comprise additional solid materials such as mineral salts, sugar or structuring soaps for example at a level of 2 to 90 wt% based on the weight of the smooth part, more preferred from 3 to 70 wt%, most preferred 5 to 40 wt%. Examples of suitable salts are for example soluble salts such as acetate, citrate, urea. The use of these materials can advantageously lead to improved structuring and/or improved dissolution properties of the smooth phase.

**[0029]** The smooth region of the tablet may also contain diluent materials for example polyethyleneglycol, dipropylenglycol, isopropanol or (mono-)propylenglycol. Preferable the level of these diluents is from 0 to 40 wt%, more preferred 1 to 20, most preferred from 4 to 40 15 wt% based on the weight of the smooth phase.

**[0030]** The smooth phase preferably comprises no or only low levels of water. Preferably the level of water is less than 20 wt % based on the weight of the smooth phase, more preferred less than 15 wt%, most preferred from 5 to 12 wt%. Most preferably the smooth phases are substantially free from water, which means that apart from low levels of moisture (e.g. for neutralisation or as crystal water) no additional added water is present.

**[0031]** Preferably the total weight of surfactants in the smooth phase is from 2 to 20 grammes, more preferred from 3 to 10 grammes.

**[0032]** Preferably the smooth phase comprises no or only low levels of ingredients such as builders, bleach activators and bleach materials. Preferably the level of 55 these ingredients in the smooth phase is less than 5 wt%.

**[0033]** In a preferred embodiment of the invention, the tablet may be a multi-phase tablet wherein the phases

other than the smooth phase as described above comprise no or only low levels of surfactants. Preferably the level of surfactants in the other phases is less than 10 wt% (based on the total weight of said phases), more preferred from 0 to 9 wt%, most preferred from 1 to 8 wt%.

**[0034]** In an advantageous embodiment of the invention the cleaning tablets comprise a first smooth region (as described above) in combination with a second region of the tablet which is a solid region, for example prepared by compression of a particulate composition.

**[0035]** Although the second region may comprise surfactant materials, this region preferably comprises ingredients of the tablet other than surfactants. Examples of these ingredients are for example builders, bleach system, enzymes etc. Preferably the builders in the tablet are predominantly present in the second region. Preferably the bleach system is predominantly present in the second region. Preferably the enzymes are predominantly present in the second region. For the purpose of this invention, unless stated otherwise, the term "predominantly present" refers to a situation wherein at least 90 wt% of an ingredient is present in the second region, more preferred more than 98 wt%, most preferred substantially 100 wt%.

**[0036]** The above description of the tablet has been given with reference to a tablet constituted by two regions. It will however be understood that each of the regions may be composed of a limited number of discrete regions. For example the first smooth region may be a single discrete part of the tablet but may also be a limited number (say 1-5) discrete smooth parts. Preferably each of these smooth parts are at least 1 gramme, also preferably each of these smooth parts is substantially of the same composition. If reference is made to the composition or weight of the first region it is understood that this concerns the total weight and composition of these smooth parts.

**[0037]** Similarly the second region may be composed of a limited number (say 1-5) of parts e.g. separate layers in the tablet. Preferably each of these parts has a weight of at least 10 grammes, also preferably each of the solid parts is substantially of the same composition. If reference is made to the composition or weight of the second region it is understood that this concerns the total weight and composition of these solid parts.

**[0038]** In addition to the smooth first region and the solid second region the cleaning tablets of the invention may optionally comprise further regions, for example the tablet may be partly or wholly coated.

**[0039]** Cleaning tablets according to the invention are preferably manufactured by firstly preparing a smooth part. Advantageously the preparation of the smooth phase may include the heating of the cleaning material followed by cooling. Advantageously the preparation of the cleaning material may involve extrusion.

**[0040]** Extrusion processes for washing articles are known, for example WO 01/02532 describes the extru-

sion of washing articles with a pressure of less than 10 bar.

**[0041]** Preferably extrusion processes will involve the forming of an extrudable mass which is then subsequently extruded from an extrusion device and optionally then partitioned into parts of the desired size and weight. Optionally the smooth parts may then be hardened.

**[0042]** The extrudable mass preferably has before extrusion an initial elevated temperature for example from 60 to 120 C, more preferred from 70 to 90 C. Preferably the extrudable mass is during the production of the smooth mass cooled e.g. to a final temperature of 20 C and then extruded. If extrusion is used this low temperature may for example be the temperature at the extrusion die for example from 10 to 40, preferably from 15 to 25, most preferred at ambient temperature (20 C).

**[0043]** In a preferred embodiment of the invention the second phase is pre-compressed at a force of 0.1 to 20 KN/cm<sup>2</sup> prior to attachment of the (partially melted) first phase thereto. In another preferred embodiment the particulate composition is flattened prior to attachment of first phase thereto.

**[0044]** Optionally the attachment of the first phase to the second phase may involve the (co-)compression of the combination of the first and the second region(s) for example at a force of from 0.05 to 20 kN/cm<sup>2</sup>. Especially if the second region has been pre-compressed the co-compression in step (c) can advantageously be at a force of 0.1- 10 kN/cm<sup>2</sup>, more preferred 0.5 to 5 kN/cm<sup>2</sup>. If the second region has not been pre-compressed, the co-compression preferably takes place at a force of 1-100 kN/cm<sup>2</sup>, more preferred 2-50 kN/cm<sup>2</sup>, most preferred 2-10 kN/cm<sup>2</sup>.

**[0045]** A tablet of this invention may be intended for use in machine dishwashing. Such a tablet is likely to contain surfactant in a low concentration such as 0.5 to 2 wt% based on the whole tablet, although higher concentrations ranging up to 10 wt% may be used. Such will typically contain salts, such as over 60 wt%, often over 85 wt% of the tablet.

**[0046]** Water-soluble salts typically used in machine dishwashing compositions are phosphates (including condensed phosphates) carbonates and silicates, generally as alkali metal salts. Water soluble alkali metal salts selected from phosphates, carbonates and silicates may provide 60 wt% or more of a dishwashing composition.

**[0047]** Another preferred possibility is that a tablet of this invention will be intended for fabric washing. In this event the tablet will be likely to contain at least 2 wt%, probably at least 5 wt%, up to 40 or 50 wt% non-soap surfactant based on the whole tablet, and from 5 to 80 wt% detergency builder, based on the whole tablet.

**[0048]** Materials that may be used in tablets of this invention will now be discussed in more detail.

## Surfactant Compounds

**[0049]** Compositions which are used in tablets of the invention will contain one or more detergent surfactants. In a fabric washing composition, these preferably provide from 5 to 50% by weight of the overall tablet composition, more preferably from 8 or 9% by weight of the overall composition up to 40% or 50% by weight. Surfactant may be anionic (soap or non-soap), cationic, zwitterionic, amphoteric, nonionic or a combination of these.

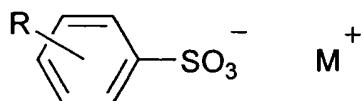
**[0050]** Anionic surfactant may be present in an amount from 0.5 to 50% by weight, preferably from 2% or 4% up to 30% or 40% by weight of the tablet composition.

**[0051]** Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

**[0052]** Primary alkyl sulphate having the formula



in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms especially 10 to 14 carbon atoms and M<sup>+</sup> is a solubilising cation, is commercially significant as an anionic surfactant.



Linear alkyl benzene sulphonate of the formula where R is linear alkyl of 8 to 15 carbon atoms and M<sup>+</sup> is a solubilising cation, especially sodium, is also a commercially significant anionic surfactant.

**[0053]** Frequently, such linear alkyl benzene sulphonate or primary alkyl sulphate of the formula above, or a mixture thereof will be the desired anionic surfactant and may provide 75 to 100 wt% of any anionic non-soap surfactant in the composition.

**[0054]** In some forms of this invention the amount of non-soap anionic surfactant lies in a range from 5 to 20 wt% of the tablet composition.

**[0055]** Soaps for use in accordance to the invention are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from beef tallow.

**[0056]** Suitable nonionic surfactant compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, ac-

ids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide.

**[0057]** Specific nonionic surfactant compounds are alkyl (C<sub>8</sub>-22) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic C<sub>8</sub>-20 primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine.

**[0058]** Especially preferred are the primary and secondary alcohol ethoxylates, especially the C<sub>9</sub>-11 and C<sub>12</sub>-15 primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

**[0059]** In some fabric washing tablets of this invention, the amount of nonionic surfactant lies in a range from 4 to 40%, better 4 or 5 to 30% by weight of the whole tablet.

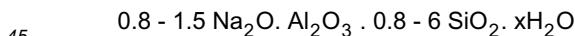
**[0060]** Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition.

**[0061]** In a machine dishwashing tablet the surfactant may be wholly nonionic, in an amount below 5 wt% of the whole tablet although it is known to include some anionic surfactant and to use up to 10 wt% surfactant in total.

## Detergency Builder

**[0062]** A composition which is used in tablets of the invention will usually contain from 5 to 80%, more usually 15 to 60% by weight of detergency builder. This may be provided wholly by water soluble materials, or may be provided in large part or even entirely by water-insoluble material with water-softening properties. Water-insoluble detergency builder may be present as 5 to 80 wt%, better 5 to 60 wt% of the composition.

**[0063]** Alkali metal aluminosilicates are strongly favoured as environmentally acceptable water-insoluble builders for fabric washing. Alkali metal (preferably sodium) aluminosilicates may be either crystalline or amorphous or mixtures thereof, having the general formula:



**[0064]** These materials contain some bound water (indicated as "xH<sub>2</sub>O") and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO<sub>2</sub> units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

**[0065]** Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well

known commercially available zeolites A and X, the novel zeolite P described and claimed in EP 384070 (Unilever) and mixtures thereof.

**[0066]** Conceivably a water-insoluble detergency builder could be a layered sodium silicate as described in US 4664839.

NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated as "SKS-6"). NaSKS-6 has the delta-Na<sub>2</sub>SiO<sub>5</sub> morphology form of layered silicate. It can be prepared by methods such as described in DE-A-3,417,649 and DE-A-3,742,043. Other such layered silicates, such as those having the general formula NaMSi<sub>x</sub>O<sub>2x+1</sub>.yH<sub>2</sub>O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used.

**[0067]** Water-soluble phosphorous-containing inorganic detergency builders, include the alkali-metal orthophosphates, metaphosphates, pyrophosphates and polyphosphates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, orthophosphates and hexameta-phosphates.

**[0068]** Non-phosphorous water-soluble builders may be organic or inorganic. Inorganic builders that may be present include alkali metal (generally sodium) carbonate; while organic builders include polycarboxylate polymers, such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates, monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono- di- and trisuccinates, carboxymethoxy-succinates, carboxymethoxymalonates, dipicolinates and hydroxyethyliminodiacetates.

**[0069]** At least one region (preferably the second region) of a fabric washing tablet preferably include polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers which can function as builders and also inhibit unwanted deposition onto fabric from the wash liquor.

#### Bleach System

**[0070]** Tablets according to the invention may contain a bleach system in at least one region of a tablet, preferably in the second region. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching action at low wash temperatures. If any peroxy oxygen compound is present, the amount is likely to lie in a range from 10 to 25% by weight of the composition.

**[0071]** Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylethylene diamine (TAED), now in wide-

spread commercial use in conjunction with sodium perborate; and perbenzoic acid precursors. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers

5 Company) are also of interest. Another type of bleach activator which may be used, but which is not a bleach precursor, is a transition metal catalyst as disclosed in EP-A-458397, EP-A-458398 and EP-A-549272. A bleach system may also include a bleach stabiliser (heavy metal sequestrant) such as ethylenediamine tetramethylene phosphonate and diethylenetriamine pentamethylene phosphonate.

**[0072]** As indicated above, if a bleach is present and is a water-soluble inorganic peroxygen bleach, the 15 amount may well be from 10% to 25% by weight of the composition.

#### Other Detergent Ingredients

**[0073]** The detergent tablets of the invention may also contain (preferably in the second region) one of the detergency enzymes well known in the art for their ability to degrade and aid in the removal of various soils and stains. Suitable enzymes include the various proteases, 25 cellulases, lipases, amylases, and mixtures thereof, which are designed to remove a variety of soils and stains from fabrics. Examples of suitable proteases are Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), and 30 Savinase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark. Detergency enzymes are commonly employed in the form of granules or marumes, optionally with a protective coating, in amount of from about 0.1% to about 3.0% by weight of the composition; and these granules or marumes present no problems with respect to compaction to form a tablet.

**[0074]** The detergent tablets of the invention may also contain (preferably in the second region) a fluorescer (optical brightener), for example, Tinopal (Trade Mark)

40 DMS or Tinopal CBS available from Ciba-Geigy AG, Basel, Switzerland. Tinopal DMS is disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene disulphonate; and Tinopal CBS is disodium 2,2'-bis-(phenyl-styryl) disulphonate.

**[0075]** An antifoam material is advantageously included (preferably in the second region), especially if a detergent tablet is primarily intended for use in front-loading drum-type automatic washing machines. Suitable antifoam materials are usually in granular form, such as 50 those described in EP 266863A (Unilever). Such antifoam granules typically comprise a mixture of silicone oil, petroleum jelly, hydrophobic silica and alkyl phosphate as antifoam active material, absorbed onto a porous absorbed water-soluble carbonate-based inorganic carrier material. Antifoam granules may be present in an amount up to 5% by weight of the composition.

**[0076]** It may also be desirable that a detergent tablet of the invention includes an amount of an alkali metal

silicate, particularly sodium ortho-, meta- or disilicate. The presence of such alkali metal silicates at levels, for example, of 0.1 to 10 wt%, may be advantageous in providing protection against the corrosion of metal parts in washing machines, besides providing some measure of building and giving processing benefits in manufacture of the particulate material which is compacted into tablets.

**[0077]** A tablet for fabric washing will generally not contain more than 15 wt% silicate. A tablet for machine dishwashing will often contain more than 20 wt% silicate. Preferably the silicate is present in the second region of the tablet.

**[0078]** Further ingredients which can optionally be employed in a region of a fabric washing detergent of the invention tablet (preferably the second region) include anti-redeposition agents such as sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl cellulose, fabric-softening agents; heavy metal sequestrants such as EDTA; perfumes; and colorants or coloured speckles.

**[0079]** Further ingredients which can optionally be used in tablets of the invention, preferably in the second region are dispersing aids. Examples of suitable dispersing aids are water-swellable polymers (e.g. SCMC) highly soluble materials (e.g. sodium citrate, potassium carbonate or sodium acetate) or sodium tripolyphosphate with preferably at least 40% of the anhydrous phase I form.

#### Particle Size and Distribution

**[0080]** The second region of a detergent tablet of this invention, is a preferably a matrix of compacted particles.

**[0081]** Preferably the particulate composition has an average particle size in the range from 200 to 2000  $\mu\text{m}$ , more preferably from 250 to 1400  $\mu\text{m}$ . Fine particles, smaller than 180  $\mu\text{m}$  or 200  $\mu\text{m}$  may be eliminated by sieving before tableting, if desired, although we have observed that this is not always essential.

**[0082]** While the starting particulate composition may in principle have any bulk density, the present invention is especially relevant to tablets made by compacting powders of relatively high bulk density, because of their greater tendency to exhibit disintegration and dispersion problems. Such tablets have the advantage that, as compared with a tablet derived from a low bulk density powder, a given dose of composition can be presented as a smaller tablet.

**[0083]** Thus the starting particulate composition may suitably have a bulk density of at least 400 g/litre, preferably at least 500 g/litre, and perhaps at least 600 g/litre.

**[0084]** Tableting machinery able to carry out the manufacture of tablets of the invention is known, for example suitable tablet presses are available from Fette and from

Korch.

**[0085]** Tableting may be carried out at ambient temperature or at a temperature above ambient which may allow adequate strength to be achieved with less applied pressure during compaction. In order to carry out the tableting at a temperature which is above ambient, the particulate composition is preferably supplied to the tableting machinery at an elevated temperature. This will of course supply heat to the tableting machinery, but the machinery may be heated in some other way also.

**[0086]** The size of a tablet will suitably range from 10 to 160 grams, preferably from 15 to 60 g, depending on the conditions of intended use, and whether it represents a dose for an average load in a fabric washing or dishwashing machine or a fractional part of such a dose. The tablets may be of any shape. However, for ease of packaging they are preferably blocks of substantially uniform cross-section, such as cylinders or cuboids. The overall density of a tablet preferably lies in a range from 20 1040 or 1050gm/litre up to 1600gm/litre.

#### Example 1

**[0087]** 1.6 kg of anionic surfactant (Dobanic acid 103 ex Shell) and 1.5 kg of nonionic surfactant (Lutensol AO7 ex BASF) were mixed and neutralised to a pH of 9 using a 50% NaOH solution.

**[0088]** 0.9 kg of C16/C18 soap fatty acid was added, 0.5 kg dipropylene glycol (ex Vopak) a,d 0.6 kg Of 30 Tween 40 (ex Uniqema) was also added to the mixture. The mixture was further neutralised with a 50% NaOH solution to a pH of 11.

**[0089]** After neutralisation to pH of 11, the mixture was pumped into a sequence of 2 stainless steel tubes by a 35 Maag Sinox P7 pump or a piston pump, type SIBa HK 05016SST4000M000 ex Prominent, Vleuten (NL). Both tubes were double jacketed. The first tube was 2.5m long and had an inner diameter of 73mm. The second tube was 1.5m long and had an inner diameter of 45mm. 40 The tubes were connected by a 10cm long pipe.

**[0090]** The mixture was pumped into the tubes at a temperature of 85°C at a throughput of 4 kg/hr. The first tube was cooled using a water bath at 40°C. The second tube was cooled using a 50:50 weight mixture of ethylene glycol and water. The coolant temperature was -15°C. The material coming out of the second tube had a temperature of about 20°C and was collected and divided into bars of around 0.5m.

**[0091]** After storage the bars can for example be cut 50 into slices of 4.9 grammes each.

#### Example II: multi-phase tablets

**[0092]** A detergent powder was made of the following 55 composition by pregranulating the granule ingredients, followed by post-dosing the rest of the ingredients

Ingredient	Parts by weight
<b>Granules</b>	
Na-las	1.1
Nonionic 7EO	0.5
C12 soap	0.1
NaAc.3aq	0.3
Zeolite A24	2.4
Light soda ash	0.4
Moisture/minors	0.4
<b>Post-dose</b>	
EAG (17% silicone)	0.8
Fluorescer (15%)	0.6
STP	8.4
Na-disilicate (80%)	1.0
TAED (83%)	1.1
Percarbonate	4.4
Dequest 2047	0.5
Minors/ enzymes/colour	to 23

Smooth parts of 4.9 grammes were prepared as in example 1

25 face; and  
C) pressing the two phases together to ensure adequate adhesion of the first smooth phase to the second phase.

5 2. A method according to claim 1, wherein the smooth phase comprises from 10 to 90 %wt of non-soap surfactants and from 0 to 20 %wt of water.

10 3. A multiphase cleaning tablet, comprising a first smooth phase having a weight of from 3 to 10 grammes and comprising a meltable material and a second phase having a weight of from 15 to 40 grammes, wherein the first smooth phase has been thermally adhered to the second phase according to the process of claim 1.

15 4. A multiphase tablet according to claim 4 wherein the second phase is a solid phase, preferably a compacted particulate phase.

20

[0093] The tablets were made as follows:

[0094] 23 grammes of the powder are inserted into a 45 mm die of a tabletting machine, followed by a compression step at 80 kN. A smooth part as described above was partially melted by applying heat to the bottom of the slice of smooth material. The heat was applied such that the bottom of the smooth phase melted, while the rest of the smooth phase did not melt. The partially melted smooth part was then placed on top of the pre-compressed phase whereby the melted surface part was used as the contact surface. The two phase were gently pressed together to ensure adequate adhesion of the smooth phase to the compressed phase.

25

30

35

40

## Claims

1. A method for the preparation of a multi-phase cleaning tablet comprising a first smooth phase having a weight of from 3 to 10 grammes and comprising a meltable material and a second phase having a weight of from 15 to 40 grammes, said method comprising the steps of

45

A) treating the outer surface of said smooth phase such that at least part of the outer surface thereof melts;

B) bringing said melted part of said smooth phase into contact with the outer surface of the second phase such that the melted surface part of the smooth phase is used as a contact sur-

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	EP 1 239 029 A (UNILEVER PLC ;UNILEVER NV (NL)) 11 September 2002 (2002-09-11) * paragraphs [0009] - [0011], [0017], [0037], [0044], [0133], [0134] * -----	1-4	C11D17/00		
X	WO 99/06522 A (PROCTER & GAMBLE) 11 February 1999 (1999-02-11) * page 5, line 27 - page 6, line 5 * * page 11, line 19 - page 12, line 2; claims 1-5,16,26,27 *	1-4			
X,D	WO 00/52127 A (HENKEL KGAA) 8 September 2000 (2000-09-08) * page 73, line 10 - page 76, line 19; claims 1,15,20 *	1-4			
A	EP 0 716 144 A (UNILEVER PLC ;UNILEVER NV (NL)) 12 June 1996 (1996-06-12) * page 7, lines 23-40; claim 1 *	1-4			
A	US 3 324 038 A (EDWARD MEYER LARRY ET AL) 6 June 1967 (1967-06-06) * column 7, lines 14,15; claims 1,5 *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.7)		
A	EP 1 090 980 A (PROCTER & GAMBLE) 11 April 2001 (2001-04-11) * paragraphs [0062], [0069], [0070], [0072], [0073] *	1-4	C11D		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
Munich	24 June 2004	Pentek, E			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document					
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document					

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 04 07 5672

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-06-2004

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1239029	A	11-09-2002	EP	1239029 A1	11-09-2002
-----					
WO 9906522	A	11-02-1999	GB	2327949 A	10-02-1999
			AT	251665 T	15-10-2003
			AT	226626 T	15-11-2002
			BR	9815605 A	20-11-2001
			CA	2298510 A1	11-02-1999
			CN	1272875 T	08-11-2000
			DE	29823752 U1	05-01-2000
			DE	29824535 U1	06-09-2001
			DE	69808885 D1	28-11-2002
			DE	69808885 T2	18-06-2003
			DE	69818871 D1	13-11-2003
			DK	960187 T3	24-02-2003
			EP	1134281 A1	19-09-2001
			EP	1162258 A2	12-12-2001
			EP	0960187 A1	01-12-1999
			ES	2206365 T3	16-05-2004
			ES	2142782 T1	01-05-2000
			JP	2001512177 T	21-08-2001
			PT	960187 T	31-03-2003
			WO	9906522 A1	11-02-1999
			US	6451754 B1	17-09-2002
-----					
WO 0052127	A	08-09-2000	AU	3159300 A	21-09-2000
			CA	2299926 A1	03-09-2000
			DE	10003429 A1	07-09-2000
			WO	0052127 A1	08-09-2000
			EP	1157090 A1	28-11-2001
-----					
EP 0716144	A	12-06-1996	EP	0716144 A2	12-06-1996
			US	5916866 A	29-06-1999
-----					
US 3324038	A	06-06-1967		NONE	
-----					
EP 1090980	A	11-04-2001	EP	1090980 A1	11-04-2001
			EP	1090981 A1	11-04-2001
-----					