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(54) **Detergent tablets**

(57) A multi-phase cleaning tablet comprising a smooth phase, wherein the smooth phase comprises at least three protruding elements having a height of from 1.0 to 7.5 mm.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to cleaning compositions in the form of tablets for use in fabric washing or machine dishwashing.

BACKGROUND OF THE INVENTION

[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 wash load.

[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 semi-solid. 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. WO 99/24549 describes a detergent tablet comprising a compressed solid body and a non-compressed gelatinous portion mounted in a mould of said body. WO99/27069 relates to a tablet comprising a compressed and a non-compressed phase, wherein the non-compressed phase improves stability of perfume components.

There also have been prior publications on form stable, solid, and/or transparent smooth or gel-like detergent compositions. In GB 1578289 such a composition comprising soap, detergent and solvent has been proposed, for detergent sticks for use in wash or dry-cleaning pretreatment. Recently it has been suggested, for example in EP 1,371,719, EP 1,405,900, EP 1,382,668, EP 1,375,636, EP 1,405,901, EP 1,405,902, EP 1,418,224 and WO 03/104380 to prepare tablets comprising a smooth or semi-solid phase.

[0005] A problem with cleaning tablets comprising a smooth phase such as for example a melt-casted, semi-solid, non-compressed or gel-like phase is often that these phases show a slow dissolution behaviour e.g. when used in a laundry washing machine. Another problem with cleaning products comprising a smooth phase is that sometimes the smooth phase sticks to the packaging material, possibly resulting in damage to the smooth part or the packaging material when unpacking the cleaning tablet. Another problem with cleaning tablets comprising a smooth phase is that some users do not like the feeling or touch of these tablets and that it is sometimes desirable to minimise contact between the user and the smooth part of the tablet.

[0006] It is an object of the present invention to provide a multi-phase cleaning tablet, comprising at least a smooth phase with a favourable dissolution rate, and/or reduced stickiness to the pack and/or reduced contact between the user and the smooth phase, whereby said cleaning tablet preferably can easily be manufactured.

DEFINITION OF THE INVENTION

[0007] In a first aspect, the invention provides a multi-phase cleaning tablet comprising a smooth phase, wherein the smooth phase comprises at least three protruding elements having a height of from 1.0 to 7.5 mm.

DETAILED DESCRIPTION

[0008] Tablets of the invention comprise a smooth phase or region. 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 can for example be semi-solid, non-compressed, gel-like or melt-casted as described above. 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.

[0009] The cleaning tablets of the invention are multi-phase tablets wherein at least one of the phases is preferably a smooth phase in the form of a layer. Preferably the tablet or the first region of the multi-phase tablet is both a smooth region and a semi-solid region. For the purpose of this invention the term semi-solid refers to compositions which are on the one hand solid enough to retain their shape at ambient temperature but which are neither completely solid. A suitable test to check if a composition can be considered as semi-solid is for example described in EP1,375,636.

[0010] The other regions of the cleaning tablet are possibly separate layers within a tablet, preferably substantially flat layers. Preferably the smooth region covers a substantial part of the upper surface of the other region, e.g. preferably at least 65%, more preferred at least 75%, most preferred more than 90% or even substantially all of the upper surface

of the other region is covered by the first smooth region. For the purpose of the invention the term upper surface refers to one of the main sides of the cleaning tablet which by placing the tablet on a flat surface could be classified as the upper surface. Especially preferably the other region of the tablet is a layer of compacted particulate material, preferably having a substantially flat upper surface.

[0011] Preferably the first smooth region is a layer having an average thickness of from 0.5 to 10 mm, more preferred 1 to 6 mm, for example 1.5 to 5 mm. Preferably the total weight the smooth region is from 1 to 40 grams, more preferred from 3 to 30 grams, most preferred from 4 to 10 Grammies, preferably the level of non-soap surfactants in the smooth region is from 0.5 to 10 grams, more preferred from 1 to 7 grams.

[0012] In a first embodiment of the invention the outer surface of the smooth phase comprises at least three, more preferably from 3 to 25 protruding elements each having a height (h) of at least 1.0 mm, more preferred from 1.0 to 7.5 mm such as 1.5 to 6 mm, most preferred from 2 to 5 mm. In a preferred embodiment, the protruding elements each have a breadth of at least 1.0 mm, for example from 1.0 to 20 mm, more preferred from 2.0 to 10 mm, most preferred from 3.0 to 7 mm.

[0013] For the purpose of the invention the term protruding element refers to parts of the smooth phase which generally have substantially the same composition as the remaining part of the smooth phase, but which preferably protrude from the outer surface of the cleaning tablet. The outer surface of the tablet may be either the upper surface of the tablet, or the lower surface of the tablet, or the upper and the lower surface of the tablet.

[0014] Preferably the protruding elements constitute from 10% to 80%, more preferred from 20% to 80%, for example from 30% to 80%, of the upper surface of the cleaning tablet.

[0015] For the purpose of the invention the breadth of the protruding element can for example be determined by measuring the top to top distance between two adjacent protruding elements. For complicated shapes for the protruding element (e.g. in case of a spirally shaped protruding element) the breadth of the protruding element may also be determined by measuring the shortest distance between two of the highest points on the protruding element. The height of a protruding element can be determined by measuring the difference in height between the highest and the lowest point of an element. Preferably the breadth of each protruding element is from 1.0 to 5.0 times its height, more preferably from 1.3 to 4.0 times its height, most preferably from 1.5 to 3 times its height.

[0016] The protruding element(s) can be of any suitable shape e.g. in the form of protruding dots (such as for example illustrated in figure 5), protruding squares, protruding shapes, logos, letters etc. Especially preferably the protruding elements are in the form of ridges, especially rounded ridges for example in the form of elongated elements present on the outer surface of the smooth phase.

[0017] Protruding elements may have any profile shape, for example rectangular ridges (for example as illustrated in fig 4a) or triangular ridges (for example as illustrated in fig 4b). Particularly preferred is the presence of rounded protruding ridges (for example as illustrated in figures 1, 2, 5 and 6), particularly rounded ridges whereby the term rounded refers to a -preferably elongated- profile element having a curved outer surface and which is preferably free from sharp angles or edges. The ridges may have any suitable form, however preferably each of the ridges is of uniform height and breadth along its (elongated) dimension. Also preferably the ridges are in close proximity to each other, whereby the breadth of each ridge is 1.5 to 4 times its height. Most preferably the ridges are touching each other such as for example illustrated in figures 1 and 2.

[0018] The number of protruding elements is at least three, preferably from 3-25, more preferred from 4-15, most preferred from 5-10. Especially preferably is the use of a tablet of circular shape comprising a number (preferably 3-10, most preferably 4-8) ridges in the form of concentric circles (as illustrated in figure 1). Also preferably the tablet is of rectangular shape and the ridges are present as from 3-15, more preferred 5-14 parallel ridges which are orientated parallel to at least one side of the tablet (for example as illustrated in figure 2). Preferably the height of each ridge is from 1.0 to 4 mm, more preferred from 1.5 to 3 mm. Preferably the breadth of each ridge is from 2.0 to 6.0 mm, more preferred from 3.0 to 5.0 mm.

[0019] Preferred embodiments of the invention will be illustrated by means of the following figures.

[0020] Figure 1 shows a preferred embodiment of a cleaning tablet of the invention whereby figure 1a shows a top-view and figure 1b shows a cross-section over the diameter d-d'. The cleaning tablet consists of a first layer (4) of compacted material on top of which is a second layer (5) of smooth material. The smooth material is arranged in the form of 6 concentric, circular rounded ridges 7 each having a breadth b and a height h.

[0021] Figure 2 shows another embodiment of the invention whereby figure 2a shows a view of the cleaning tablet from above and figure 2b shows a cross-section over the line p-p'. The cleaning tablet consists of a first layer of compacted material (8) on top of which is a second layer (9) of smooth material. The smooth material is arranged in the form of 11 parallel rounded ridges each having a breadth b and a height h.

[0022] Figure 3 shows a cross-section of a mould arrangement for preparing a smooth part for use according to the present invention. As shown in Figure 3, a mould arrangement for manufacturing a tablet part in accordance with the process according to the present invention comprises a mould 1, under which is situated a piston 3. Reference number 5 depicts a smooth part of a laundry cleaning tablet.

[0023] The mould 1 comprises a peripheral wall 7, which is ring shaped and bounds a space 9. The space 9 is bridged by a diaphragm 11. The peripheral wall comprises two parts. The first is an annular support ring 13 having L-shaped cross-section. The support ring 13 is made of aluminium. Received within this L-shaped support ring 13, is a silicone rubber insert 15 which comprises the diaphragm 11 and integral therewith, an annular peripheral support 17 therefor. The silicone rubber has a shore hardness in the range 40 - 55. The peripheral support is wall comprising the support ring 13 and the peripheral support 17.

[0024] The space 9 within the peripheral wall 7 is divided by the diaphragm 11 which joins the peripheral support 17 at a position approximately 1/3 of the distance between the upper rim 19 and the lower rim 21 of the peripheral wall 7. The diaphragm 11 is provided with a profile substantially corresponding to the forming of a number of circular rounded ridges for the smooth part as illustrated in figure 1 (not shown).

[0025] The space 9 divided by the diaphragm 11 thereby provides an upper cavity 23 above the diaphragm 11 and a lower cavity 25 below the diaphragm.

[0026] As shown in Figure 3, the diaphragm 11 is slightly bowed so as to be concave when viewed from above, into the upper cavity 23. In use, a molten composition is poured into the upper cavity 23 and allowed to cool to ambient temperature whereupon, it adopts a semi-solid smooth consistency to form the tablet parts. Once sufficient solidification has been achieved, the tablet part formed in this way is ejected by action of the piston 3, which sits within the lower cavity 25, being moved upwardly to distort the diaphragm 11 so that it becomes flat and/or convex when viewed from the direction of the upper cavity 23. The tablet part is thereby ejected and conveyed away. The mould can then be refilled in the same way for repeat use.

[0027] To facilitate ejection and inhibit clinging of the semi-solid composition to the mould, the side wall 27 of the upper cavity 23, which side wall is defined by an inner surface of the peripheral support 17, adjacent to the upper rim 19, is outwardly angled relative to the axis of symmetry 29 of the mould, such as to make an angle θ which is approximately 10° to the vertical.

[0028] Figure 4A shows a cross-section of a rectangular cleaning tablet comprising a phase of compacted particulate material (40) and a smooth phase 41 which comprises 6 elongated rectangular ridges orientated parallel to and along the entire side of the tablet (not shown). The ridges constitute about 55% of the upper surface of the tablet.

[0029] Figure 4B shows a cross-section of a rectangular cleaning tablet comprising a phase of compacted particulate material (40) and a smooth phase composed of 6 triangular elongated ridges orientated parallel to one side of the tablet. The ridges cover about 90% of the upper surface of the tablet.

[0030] Figure 5A shows a top view of a circular cleaning tablet comprising a smooth phase which is constituted by 13 protruding dots covering about 40% of the upper surface of the cleaning tablet.

[0031] Figure 5B shows a cross-section of the tablet of figure 5A along the line K-K'. The tablet has a phase of compacted particulate material (44) on top of which is a smooth phase constituted by rounded circular protruding dots (45).

[0032] Figure 6 shows a top-view of a cleaning tablet comprising a first layer of compacted particulate material (not shown) on top of which is a smooth phase in the form of a single spiral-shaped protruding element formed by a single elongated rounded strand of smooth material. The cross-section along line d-d' is similar to the cross-section along d-d' in figure 1A. The number of protruding elements in this case is equal to the number of ridges in the cross-section over the diameter d-d'.

[0033] In an advantageous embodiment of the invention the smooth or semi-solid first region comprises from 40-100 wt% of non-soap surfactants (based on the total weight of the smooth region), more preferred from 50-95 wt%, most preferred the first region is predominantly constituted by non-soap surfactants e.g. more than 55 wt% for example 56 to 90 wt%. It has been found that the combination of a separate smooth or semi-solid region and these high surfactant levels provide very good dispersing and cleaning properties to the tablet.

[0034] In a preferred embodiment the surfactants in the smooth region comprise a combination of anionic surfactants and non-soap 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. In another preferred embodiment the smooth region comprises relatively high levels of non-ionic surfactants, preferably the non-soap surfactants are predominantly non-ionic surfactants, most preferred all the non-soap surfactants are non-ionic surfactants. Further surfactants, for example cationic surfactants may equally be present for example at a level of 0.1 to 10 wt% based on the weight of the smooth or semi-solid part.

[0035] Also advantageously the smooth or semi-solid region may comprise soap for example at a level of 0.1 to 10 wt% based on the weight of the smooth or semi-solid part. Especially preferably the soap is present in a level of at least 1 wt% of the smooth phase. In a very preferred embodiment of the invention the level of C16 soaps is relatively high, particularly it is preferred that at least 50 wt% of the soap is a C16 soap, even more preferred from 60 to 100 wt% of the soap is a C16 soap.

[0036] Also advantageously the first smooth region of the tablet comprises at least 5 wt% of diluent materials having a dielectric constant from 5 to 16. Also preferably the molecular weight of the diluents is from 50 to 250, e.g. from 100 to 200. Preferred examples of diluents are for example, Tri-ethyleneglycol di-methyl ether or Di-(Ethylene Glycol)Ethyl ether or mixtures thereof. Preferably the level of the diluents is from 5 to 40 wt%, more preferred 2 to 30, most preferred

10-25 wt% based on the weight of the smooth region. Also preferably the diluents used in the smooth phase preferably have a flashpoint of at least 75°C, most preferred above 80°C or even above 90°C.

[0037] The smooth or semi-solid 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 semi-solid phase, more preferred less than 15 wt%, most preferred from 5 to 12 wt%. Most preferably the smooth or semi-solid 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.

[0038] Preferably cleaning tablets in accordance to the invention also comprise a second region or phase which is a solid region preferably a region of compacted material. The weight of the solid region may suitably range from 1 to 60 grams, more preferred from 10 to 50 grams, most suitably from 20 to 40 grams.

[0039] In a preferred embodiment of the invention the second region comprises no or only low levels of surfactants. Preferably the level of surfactants in the second region is less than 10 wt%(based on the total weight of the second region), more preferred from 0 to 9 wt%, most preferred from 1 to 8 wt%.

[0040] The second region of the tablet is preferably a solid region, for example this can be prepared by compression or melting. Preferably the second region is a compacted particulate composition. The second region preferably comprises ingredients of the tablet other than surfactants. Examples of these ingredients are 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 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%.

[0041] Materials which may be used in tablets of this invention will now be discussed in more detail.

Surfactant Compounds

[0042] 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.

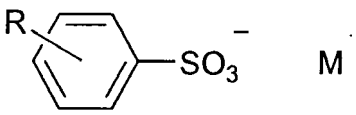
[0043] Anionic surfactant may be present in an amount from 0.5 to 50% by weight, preferably from 2% or 4% up to 30% or 40% by weight of the tablet composition.

[0044] Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkyl-benzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0045] Primary alkyl sulphate having the formula

$$ROSO_3^- M^+$$

in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms especially 10 to 14 carbon atoms and M^+ 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^+ is a solubilising cation, especially sodium, is also a commercially significant anionic surfactant.

[0046] 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.

[0047] 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.

[0048] 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.

[0049] 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, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide.

[0050] Specific nonionic surfactant compounds are alkyl (C_{8-22}) phenol-ethylene oxide condensates, the condensation

products of linear or branched aliphatic C_{8-20} 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.

[0051] Especially preferred are the primary and secondary alcohol ethoxylates, especially the C_{9-11} and C_{12-15} primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

[0052] 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.

[0053] Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition.

[0054] 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

[0055] 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.

[0056] 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:

$$0.8 - 1.5\ Na_2O.Al_2O_3.\ 0.8 - 6\ SiO_2.\ xH_2O$$

[0057] These materials contain some bound water (indicated as "xH_2O") 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_2 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.

[0058] 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.

[0059] 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_2SiO_5 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 $NaMSi_xO_{2x+1}.\ yH_2O$ 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.

[0060] 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 hexametaphosphates.

[0061] 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, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates and hydroxyethyliminodiacetates.

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

[0062] 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 peroxygen compound is present, the amount is likely to lie in a range from 10 to 25% by weight of the composition.

[0063] 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 widespread commercial use in conjunction with sodium perborate; and perbenzoic acid precur-

sors. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers 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.

[0064] As indicated above, if a bleach is present and is a water-soluble inorganic peroxygen bleach, the amount may well be from 10% to 25% by weight of the composition.

Other Detergent Ingredients

[0065] 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, 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 DSM N.V., Delft, Netherlands, and Alcalase (Trade Mark), and Savinase (Trade Mark), as supplied by Novozymes 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.

[0066] The detergent tablets of the invention may also contain (preferably in the second region) a fluorescer (optical brightener), for example, Tinopal (Trade Mark) DMS or Tinopal CBS available from Ciba Speciality Chemicals 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-(phenylstyryl) disulphonate.

[0067] 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 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.

[0068] 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.

[0069] 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.

[0070] Further ingredients which can optionally be employed in a region of a fabric washing detergent of the invention tablet (preferably the second region) include antiredeposition 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.

[0071] 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 tripolyphospate with preferably at least 40% of the anhydrous phase I form.

[0072] The above description of the tablet has been given with reference to a tablet constituted by one or two regions. It will however be understood that each of the regions may be composed of a limited number of discrete regions such as for example illustrated in figure 5.

[0073] Cleaning tablets of the invention may be manufactured by any suitable method e.g. the pre-preparation of the smooth phase e.g. by extrusion or melt-casting followed by assembly of the smooth phase and the other phases of the tablet. Also the second phase of compressed particulate material may be pre-prepared followed by in-situ preparation of the smooth phase e.g. by casting, coating or spraying, or assembly of said compressed phase with a separately prepared smooth phase. Typical processing conditions for preparing the smooth phase or the compressed phase are for example disclosed in the documents as described above.

[0074] A preferred process for the preparation of a cleaning tablet of the invention is described in EP 1,371,721 and involves the separate preparation of a smooth phase, preferably by a casting process. Also separately a solid layer is formed preferably by a compression step, followed by assembly of the smooth phase and the solid layer. Especially preferably the process of the invention involves the preparation of the smooth phase by casting wherein a mould is used which is at least partially made of a flexible material for example as described in our non-prepublished patent application EP04076395.5. Especially preferably the bottom part of the mould is made of flexible material. The shape of this mould

preferably corresponds to the desired profile of rounded ridges for the smooth phase. The material forming the smooth phase can be introduced into the at least partially flexible mould thus forming a smooth phase having a ridged side adjacent to the mould and a substantially flat upper side. The smooth phase is then optionally rested to set, followed by optionally turning the mould up side down and flexing the flexible bottom part of the mould, thereby releasing the smooth part from the mould. Subsequently the smooth part can be assembled with the compressed phase e.g. by using a glue or barrier layer between the smooth phase and the solid phase, whereby the substantially flat side is adhered to the solid phase thus exposing the protruding elements the smooth phase.

[0075] The use of an at least partially flexible mould, provided with a profile corresponding to the formation of a smooth phase, and having the above described number of rounded ridges has the additional advantage that the presence of a "mirror-image" ridged profile in the mould allows a remarkably easy release of the smooth part from the mould, while leaving an advantageously low level of residues in the mould.

[0076] Tablets of the invention may be used e.g. for mechanical diswashing or laundry washing. For this purpose generally 1-5 tablets will be used per wash where appropriate a dispenser e.g. a shuttle or a net may be used.

[0077] The invention will be further illustrated by means of the following examples.

EXAMPLES

Example 1

[0078] Smooth or semi-solid parts were prepared of the following composition:

Ingredient	*Parts by weight*
Na-LAS	5.3
Nonionic 5EO	5.3
C12 soap	0.5
Tween 40	2.0
Dipropyleneglycol	4.2

[0079] Smooth parts P and Q of 5 g each and having a shape as in figure 1 where produced by heating the composition to 80°C and casting into moulds as shown of figure 3 and cooled to 20°C to form firm, 5 grams smooth and semi-solid parts of about 32 mm diameter and about 6mm high having one substantially flat side and one side comprising 6 circular rounded ridges each having a width of about 3 mm and a height of about 2.5 mm as shown in figure 1. The flat (non-ridged) bottom surface of smooth part Q was provided with 0.5 gram of an adhesive material (sulphonated polyester; Bostik Findley HX 9393).

[0080] As a comparison the smooth part formulation was used to prepare smooth parts of composition R (without adhesive) and composition S (with 0.5 g adhesive) which did not have rounded ridges. These smooth parts had two substantially flat sides, a weight of approximately 5 g smooth material(plus 0.5 gram adhesive for composition S), a diameter of about 32 mm and a height of about 5mm.

[0081] The dissolution properties of the parts were determined by adding a single smooth part to 500 ml of water at 20 C, followed by stirring for 5 minutes at 100 rpm. Any remaining adhesive material was removed and the residual weight of the non-dissolved smooth part was determined and the percentage of dissolved matter based on the original weight of the 5 Grams smooth formulation (excluding the adhesive material) was calculated.

[0082] The following results were obtained

Wt% of smooth material dissolved after 5 minutes

P (ridged shape without adhesive) 45 %

Q (ridged shape with adhesive) 27 %

R (flat shape without adhesive) 38 %

S (flat shape with adhesive) 18 %

Example 2

[0083] A detergent powder was made of the following composition by pre granulating the granule ingredients, followed by post-dosing the rest of the ingredients

Ingredient	Parts by weight
granules	
Na-LAS	1.1
Nonionic 7EO	0.5
Soap (C16-C18)	0.1
Zeolite A24	2.4
NaAc3aq	0.3
Light soda ash	0.4
SCMC (68%)	0.1
Moisture/minors	0.4
Post-dose	
EAG (17% silicone)	3.0
Fluorescer (15%)	2.2
STP HPA	28.3
STP LV	34.0
Na-disilicate (80%)	3.8
TAED (83%)	4.3
Percarbonate	16.9
Dequest 2047	1.9
Minors/ enzymes/colour	to 100

[0084] Multi-layer tablets are made by pre-compressing 25 grams of the powdered composition in a die of 35 mm diameter at 4 kN/cm^{2,} way followed by applying 0.5 grams of adhesive (sulphonated polyester) on top of the compressed phase followed by adherence of a smooth and semi-solid part according to P of example 1 on top of the compressed layer.

Example 3

[0085] Example 2 was repeated by replacing the detergent powder by a powder of the following composition whereby the ingredients marked with an * were pre granulated followed by post-dosing the remaining ingredients.

Tablet	**Parts by weight**
Zeolite A24 *	21
Na-LAS *	9.3
Soap (C16018)*	0.7
Nonionic 7EO *	4.1
Sodium acetate trihydrate*	2.7
Sodium percarbonate (coated)	18
TAED	8.1
Sodium disilicate	5.1
Sodium acetate 3aq	27.0
moisture	4.0

Example 4

[0086] Example 2 was repeated by using instead of the smooth part P of example 1 a smooth part with a composition as in example 1, but with a shape in accordance to one of figures 4A, 4B, 5 or 6.

Claims

1. A multi-phase cleaning tablet comprising a smooth phase, wherein the smooth phase comprises at least three protruding elements having a height of from 1.0 to 7.5 mm.

2. A cleaning tablet according to claim 1, wherein the at least three protruding elements protrude from an outer surface of the tablet.

3. A cleaning tablet according to any of the preceding claims, wherein the smooth phase comprises 3 to 25 protruding elements.

4. A cleaning tablet according to any of the preceding claims, wherein the protruding elements are rounded ridges.

5. A cleaning tablet according to any of the preceding claims, which is of circular shape comprising 4-10 protruding elements in the form of concentric circles.

6. A cleaning tablet according to any of claims 1-4, which is of rectangular shape and the protruding elements are present as from 6-15 parallel ridges which are orientated parallel to one side of the tablet.

7. A tablet according to any of the preceding claims wherein the height of each protruding element is from 1 to 4 mm, more preferred from 1.5 to 3 mm and the breadth of each protruding element is from 2.0 to 6.0 mm, more preferred from 3.0 to 5.0 mm.

8. A cleaning tablet according to claim 1 comprising a phase of compacted particulate material in addition to a smooth phase.

Figure 1,

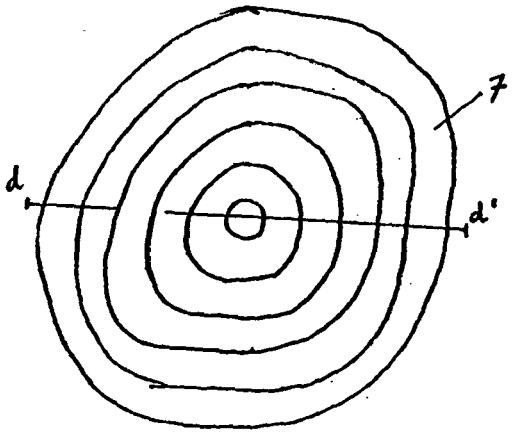
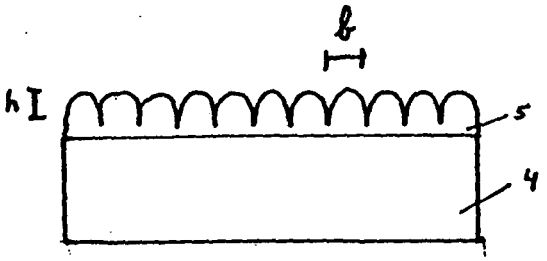


fig 1A



f1.b

Figure 2.

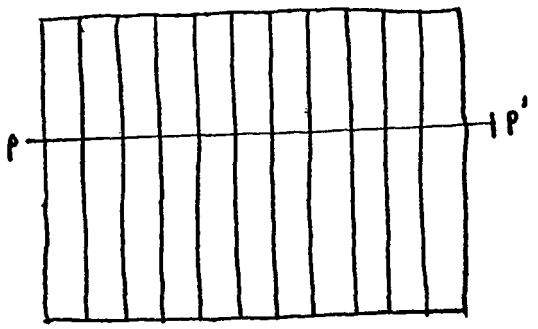


Fig 2a

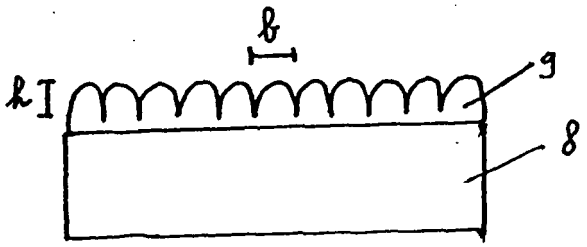


Fig 2b

Figure 3

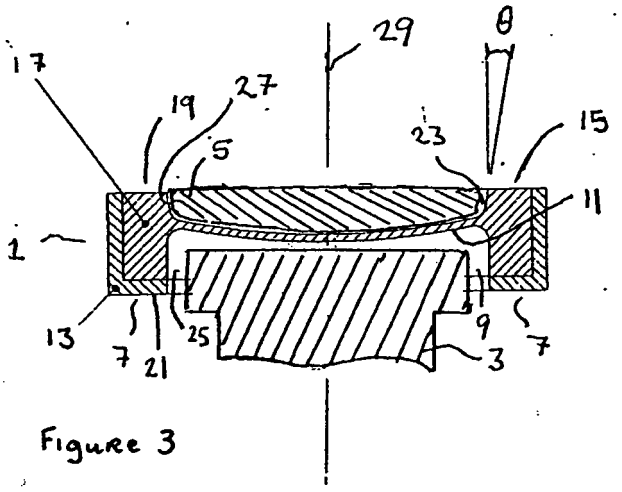


Figure 3

Figure 4

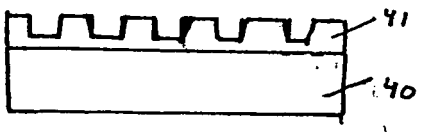


Figure 4A

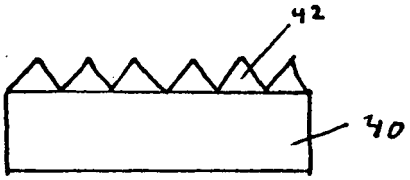


Figure 4B

Figure 5,

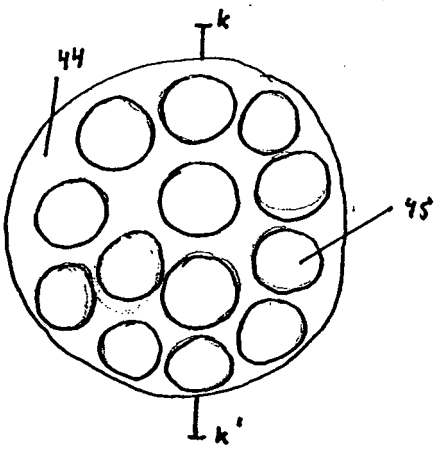


Figure 5a

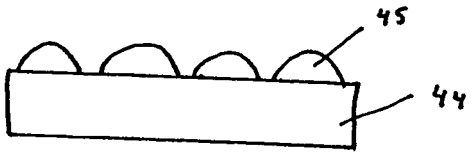


Figure 5b

Figure 6,

Figure 6

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EUROPEAN SEARCH REPORT

Application Number
EP 06 07 5874

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	DE 103 13 172 A1 (HENKEL KGAA) 14 October 2004 (2004-10-14) * paragraphs [0003], [0005], [0010], [0011], [0015], [0016]; claims 1,2,5-8 *	1-8	INV. C11D17/00
Y	EP 1 382 668 A (UNILEVER N.V; UNILEVER PLC) 21 January 2004 (2004-01-21) * paragraphs [0008], [0014]; claim 1 *	1-8	
Y	US 5 198 140 A (JOSHI ET AL) 30 March 1993 (1993-03-30) * column 1, lines 11-13,52-60; figures 2,5,6 *	1-8	
Y	US 4 996 000 A (REDEKER ET AL) 26 February 1991 (1991-02-26) * column 1, lines 6-8; figures 3,5,6 *	1-8	
Y	DE 199 08 057 A1 (HENKEL KGAA) 31 August 2000 (2000-08-31) * page 2, lines 34-38,61-66; claims 1-10 * * page 3, lines 1-10,28-30 *	1-8	TECHNICAL FIELDS SEARCHED (IPC) C11D
A	DE 199 30 771 A1 (HENKEL KGAA) 4 January 2001 (2001-01-04) * column 2, lines 53-66; figures 3,13,14,10,25,26,35,41 * * page 3, lines 1-10,28-30 *	1-8	
A	EP 1 491 622 A (UNILEVER N.V; UNILEVER PLC) 29 December 2004 (2004-12-29) * paragraph [0008]; figure 3 *	1-8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 July 2006	Klier, E

CATEGORY OF CITED DOCUMENTS

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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
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28-07-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 10313172 A1	14-10-2004	EP 1606382 A1	21-12-2005
		WO 2004085595 A1	07-10-2004
EP 1382668 A	21-01-2004	NONE	
US 5198140 A	30-03-1993	NONE	
US 4996000 A	26-02-1991	NONE	
DE 19908057 A1	31-08-2000	AU 3155100 A	14-09-2000
		CA 2300018 A1	25-08-2000
		WO 0050558 A1	31-08-2000
DE 19930771 A1	04-01-2001	AT 265522 T	15-05-2004
		AU 5406700 A	22-01-2001
		CA 2313356 A1	03-01-2001
		WO 0102532 A1	11-01-2001
		EP 1192241 A1	03-04-2002
		ES 2220474 T3	16-12-2004
EP 1491622 A	29-12-2004	DE 60302878 T2	20-07-2006
		ES 2254862 T3	16-06-2006

EPO FORM P0459

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 0142416 A **[0004]**
- WO 0061717 A **[0004]**
- WO 0004129 A **[0004]**
- WO 9924549 A **[0004]**
- WO 9927069 A **[0004]**
- GB 1578289 A **[0004]**
- EP 1371719 A **[0004]**
- EP 1405900 A **[0004]**
- EP 1382668 A **[0004]**
- EP 1375636 A **[0004] [0009]**
- EP 1405901 A **[0004]**
- EP 1405902 A **[0004]**
- EP 1418224 A **[0004]**
- WO 03104380 A **[0004]**
- GB 1429143 A **[0058]**
- EP 384070 A **[0058]**
- US 4664839 A **[0059]**
- DE 3417649 A **[0059]**
- DE 3742043 A **[0059]**
- US 4751015 A **[0063]**
- US 4818426 A **[0063]**
- EP 458397 A **[0063]**
- EP 458398 A **[0063]**
- EP 549272 A **[0063]**
- EP 266863 A **[0067]**
- EP 1371721 A **[0074]**
- EP 04076395 A **[0074]**