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(54) Detergent compositions

(57) A cleaning tablet comprising a smooth or semi-solid phase wherein the smooth or semi-solid phase comprises:

(a) from 10 to 90 wt% of non-soap surfactants; and
(b) from 2 to 75 wt% of soap;
(c) from 5 to 50 wt% a material selected from poly-alkoxylated carbohydrates and stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0; and
(d) from 0 to 20 wt% of water

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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 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.

[0005] It is an object of the present invention to provide a method to produce cleaning tablet comprising smooth or a semi-solid phase, wherein said smooth or semi-solid phase comprises surfactants and wherein said cleaning tablet has good dispersing properties of the smooth or the semi-solid phase and wherein the smooth or semi-solid phase has preferably a suitable texture (between soft and hard).

[0006] A further objective of the present invention is to provide a method to produce a smooth or semi-solid 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] Although the invention can relate to a single phase smooth or semi-solid tablet, according to a preferred embodiment of the present invention there is provided 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 or semi-solid region and at least one second region of the tablet is a solid region of compacted particulate material.

[0008] In a first aspect the invention relates to a cleaning tablet comprising a smooth or semi-solid phase wherein the smooth or semi-solid phase comprises:

(a) from 10 to 90 wt% of non-soap surfactants; and
(b) from 2 to 90 wt% of soap;
(c) from 2 to 30 wt% of a material selected from polyoxyalkoxylated carbohydrates or stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0 and polyoxypropylated carbohydrates; and
(d) from 0 to 20 wt% of water.

[0009] Preferably tablets of the invention are of cylindrical shape wherein the two main surfaces (upper side and bottom side) are substantially flat.

[0010] As indicated above, tablets of the invention can be single phase tablets, which are predominantly constituted by the semi-solid phase as described above. However a preferred embodiment of the invention relates to a multiphase tablet wherein the smooth or semi-solid phase is present and additionally one or more other phases are present. Suitably these additional phases can be smooth, semi-solid or solid. Particularly suitable are solid phases composed of compacted particulate solids.

[0011] The regions of a multi-phase tablet are possibly 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 or semi-solid 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 or semi-solid material embedded in the second region which is a layer of compacted particulate material.

[0012] If the tablet is a single phase smooth or semi-solid tablet, then preferably the weight of this tablet will be from 5 to 100 g, more preferably from 10 to 40 g, most preferably from 15 to 35 g.

[0013] If the tablet is a multi-phase tablet comprising the smooth or semi-solid phase of the invention then preferably the smooth or semi-solid phase is present as a distinctive region preferably having a weight of from 2 to 20 grammes, more preferred from 3 to 10 grammes. Preferably the other phases together have a weight of 10 to 50 grammes, more preferred 15 to 40 grammes.

[0014] 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 ot 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.

[0015] 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 not completely solid. Semi-solid phases generally have a smooth non-porous appearance.

[0016] A suitable test to check if a composition can be considered as semi-solid can be described as follows.

[0017] A cylindrical tablet with a diameter of 45 mm and a height of 20 mm is compressed radially between the plates of a material testing machine until the tablet fractures. At the starting position the plates contact the tablet but do not apply force to it. Force is applied to compress the tablet, the vertical speed of the upper plate is 25 mm/minute. The testing machine measures the applied force (F), and also the displacement (x) of the plates towards each other as the tablet is compressed. The distance (y) between the plates before force is applied, which is the diameter of the tablet, is also known. At failure, the tablet cracks and the applied force, needed to maintain the displacement, drops. Measurement is discontinued when the applied force needed to maintain the displacement has dropped by 25% from its maximum value. The displacement at failure (x_f) is measured.

[0018] A graph of force (F) against displacement (x) will be made. The maximum force is the force at failure (F_f). The break energy is the area under the graph of force against displacement, up to the point of break, is given by the equation:

$$E_b = \int_{0}^{-x_f} F(x)\ dx$$

wherein E_b is the break energy in mJoules, x is the displacement in metres and F is the applied force in Newtons at displacement x and x_f is the displacement at failure.

[0019] Semi-solid compositions are characterised by a ratio of F_f to E_b of less than 1.0, more preferred from 0.1 to 0.9, most preferred from 0.2 to 0.6, while traditional tablets of compacted particulate materials are generally characterised by a ratio of F_f to E_b of more than 1, more generally more than 1.25 or even more than 1.5 up to say 6.

[0020] Preferably the tablets of the invention comprise a phase which is both smooth and semi-solid. However sometimes a smooth (non semi-solid) phase may equally be suitable.

In an advantageous embodiment of the invention the smooth or semi-solid phase comprises from 20-80 wt% of non-soap surfactants (based on the total weight of said semi-solid phase), more preferred from 25 to 75 wt%, most preferred 30 to 70 wt%. It has been found that the combination of a separate smooth or semi-solid first region and these high surfactant levels provide very good dispersing and cleaning properties to the tablet.

[0021] Preferably the non-soap surfactants in the first 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 of 0.1 to 10 wt% based on the weight of the smooth or semi-solid part.

[0022] In addition to the non-soap surfactants the smooth or semi-solid region will comprise soap for example at a level of 2 to 90 wt% based on the weight of the smooth or semi-solid part, more preferred from 3 to 70 wt%, most preferred 5 to 40 wt%.

[0023] It has been found that the soap provides good structuring properties to the smooth or semi-solid phase, especially if this phase comprises relatively high levels of surfactants. This structuring leads on the one hand to a desired firm consistency of the semi-solid phase but on the other hand retains the smooth or semi-solid nature of the phase. Furthermore the soap is capable of reducing the bleeding of the smooth or semi-solid phase.

[0024] The smooth or semi-solid region of the tablet will also contain at least 5 wt% of a material selected from polyalkoxylated carbohydrates and stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0.

[0025] Examples of suitable polyalkoxylated carbohydrates are carbohydrates comprising from 2 to 10 hydroxy groups (generally 2 to 8 hydroxy groups, more general 2 to 6 hydroxy groups) of which at least 2 are alkoxylated preferably ethoxylated or propoxylated or ethoxy/propoxylated (generally 2 to 4 hydroxy groups are alkoxylated) with on average 2-20 ethoxy and or propoxy groups (generally 4 to 14 groups per alkoxylated hydroxy group, more generally from 5 to 10). The carbohydrates may be advantageously be polyols such as glycerol, sugars and sugar-like materials such as sorbitol. Also the carbohydrates may be esterified with preferably one fatty acid groups.

[0026] Examples of preferred alkoxylated carbohydrate materials are polyoxyethylene-sorbitan mono-fatty esters (for example Tween 20, Tween 40 and Tween 60), polyoxyethylene-sorbitol fatty esters (for example Atlas G4895, Atlox 1045A), polyoxyethylene glycerol esters (for example Atlas G7074), polyoxyethylene glyceril sorbitan isostearate (for example Arlacel 582), polyoxyethylene-hexitan-fatty esters (for example Arlacel 121), polyoxyethylene sorbitan (for example obtainable by hydrolysing Tween 20, Tween 40 and Tween 60), polyoxyethylene-sorbitol, polyoxyethylene glycerol, polyoxyethylene glycerol sorbitan, polypropoxylated sorbitan (for example Atlas G2320, G2330 and G2401).

[0027] Examples of stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0. are described in EP 328 177 and EP 359 308. Especially preferably the stabilising surfactants have a salting out resistance of greater than or equal to 4.0, most preferred greater than or equal to 5.0 generally the salting out resistance will be less than 40 or even 20. Especially preferred are alkyl poly alkoxylated carboxylates, alkyl polyalkoxylated phosphates, alkyl polyalkoxylated sulphosuccinates, dialkyl diphenyl oxide disulphonates and alkyl polysaccharides.

[0028] The level of the material selected from polyalkoxylated carbohydrates and stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0 (based on the total weight of the semi-solid region is preferably from 5 to 50 wt%, more preferred 10 to 45 wt%, most preferred 15 to 40 wt%.

[0029] The smooth or semi-solid region of the tablet may also contain diluent materials for example polyethyleneglycol preferably having a molecular weight of less than 5000 or even less than 1000, dipropyleneglycol, isopropanol or (mono-)propyleneglycol. Preferably the level of these diluents is from 0 to 50 wt%, more preferred 5 to 45, most preferred from 15 to 40 wt% based on the weight of the smooth or semi-solid phase.

[0030] The smooth or semi-solid phase 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.

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

[0032] In a preferred embodiment of the invention the tablet may be a multi-phase tablet wherein the phases other than the smooth or semi-solid phase as described above comprise no or only low levels of surfactants. Preferably the level of surfactants in the 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%.

[0033] In an advantageous embodiment of the invention the cleaning tablets comprise a first smooth or semi-solid 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.

[0034] 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%.

[0035] 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 or semi-solid region may be a single discrete part of the tablet but may also be a limited number (say 1-5) discrete smooth or semi-solid parts. Preferably each of these smooth or semi-solid parts are at least 1 gramme, also preferably each of these smooth or semi-solid 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 or semi-solid parts.

[0036] Similarly the solid second region may be composed of a limited number (say 1-5) of solid 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.

[0037] In addition to the smooth or semi-solid 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.

[0038] Cleaning tablets according to the invention are preferably manufactured by firstly preparing a smooth or semi-solid part. Advantageously the preparation of the smooth or semi-solid phase may include the heating of the ingredients followed by cooling. Advantageously the preparation of the smooth or semi-solid phase may involve extrusion.

[0039] Extrusion processes for washing articles are known, for example WO 01/02532 describes the extrusion of washing articles with a pressure of less than 10 bar.

[0040] Preferably extrusion processes for preparing the smooth or semi-solid parts for use in tablets of the invention will involve the forming of an extrudable mass which is then subsequently extruded from an extrusion device and optionally then partioned into parts of the desired size and weight. Optionally the semi-solid parts may then be hardened.

[0041] The extrudable mass preferably has 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 or semi-solid mass cooled e.g. to a final temperature of 20 C. 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).

[0042] In a very preferred embodiment of the invention the conditions for extrusion are carefully controlled. In particular it has been found that semi-solid parts which on the one hand contain relatively high levels of soap and non-soap surfactants and on the other hand have the right textural properties (i.e not too soft and of semi-solid character) can advantageously be produced by an extrusion process wherein no high-shear conditions are applied, in particular under cooling. Particularly it is preferred that the the extrusion takes place under low-shear conditions in the extrusion device. Suitable extrusion devices for this purpose are for example free from extrusion screws. Especially preferred is the feeding of the extrudable mass to a elongated chamber e.g a pipe provided with cooling means but not provided with stirring or shearing devices.

[0043] After the production of the smooth or semi-solid part the cleaning tablet of the invention may advantageously be made by a process comprising the steps of:

(a) compressing a particulate composition int a tablet mould
(b) combining one or more smooth or semi-solid parts with the compressed particulate composition.

[0044] In a preferred embodiment of the invention the particulate composition is compressed at a force of 0.1 to 100 kN/cm^2.

[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 which 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.

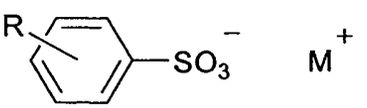
[0050] Anionic surfactant may be present in an amount from 0.5 to 50% by weight, preferably from 2% or 4% up to 30% or 40% by weight of the tablet composition.

[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_8-C_{15}; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0052] 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.

[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 coconut oil, beef tallow, sunflower or hardened rapeseed oil. Especially preferably soaps are selected from C_{10} to C_{20} soaps for example from C_{16} to C_{18} or C_{12} soaps.

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

[0057] 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.

[0058] 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.

[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:

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

[0064] These materials contain some bound water (indicated as "xH2O") 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.

[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_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.

[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 hexametaphosphates.

[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, carboxymethyloxysuccinates, carboxymethyloxymalonates, 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 peroxygen 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 widespread 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 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 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, 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 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) 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 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 tripolyphospate 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 μm, more preferably from 250 to 1400 μm. Fine particles, smaller than 180 μm or 200 μm 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 1040 or 1050gm/litre up to 1600gm/litre.

Example 1

[0087] 7 kg of anionic surfactant (Dobanic acid 103 ex Shell) and 6kg of nonionic surfactant (Neodol 1-5) were mixed and neutralised to a pH of 9 using a 50% NaOH solution.

[0088] Soap fatty acid (ex Uniqema), diluent dipropylene glycol (ex Vopak) and ethoxylated materials were added to the mixture in the amounts as indicated in the table. The mixture was kept at a temperature around 80°C until the fatty acid had dissolved and then 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 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. The tubes were connected by a 10cm long pipe.

[0090] The extrusion was performed via die-head (with inner diameters of resp 24 and 32 mm), which was attached to the second tube.

[0091] 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.

[0092] After storage the bars were cut into smooth and semi-solid cylindrical slices (18mm diameter) of comparable quality and 5 gramme each.

[0093] The dissolution of the slices was determined by immersing a piece into 500 ml tap water at 20 C, stirring at 200 rpm and measuring the remaining weight of the slices at 3 or 5 minute intervals. t80 (the time by which 80% of the mass of the test piece has dissolved was determined.

[0094] The following results were obtained.

Formulations (all levels are dosed on top of the anionic/nonionic mixture) and t80 in minutes.				
	Adjunct (%)	DPG (%)	C12 soap(%)	t80 (min)
A (comp)	0	0	25	>35
B	50 (Tween 40)	0	25	25
C	25 (Tween 40)	25	25	18
D	25 (Atlas G2330)	25	25	27

Example II: multi-phase tablets

[0095] A detergent powder was made of the following composition by pregranulating 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
C12 soap	0.1
NaAc.3aq	0.3
Zeolite A24	2.4
Light soda ash	0.4
Moisture/minors	0.4
Post-dose	
EAG (17% silicone)	3.0
Fluorescer (15%)	2.2
STP	62.4
Na-disilicate (80%)	3.8
TAED (83%)	4.3
Percarbonate	16.9
Dequest 2047	1.9
Minors/ enzymes/colour	to 100

Smooth or semi-solid parts of 5 gramme were prepared as in example 1

[0096] The tablets were made in 2 different ways:

(I) 20 grammes of the powder are inserted into a 45 mm die of a tabletting machine, optionally followed by a flattening step, followed by addition of a single semi-solid part on top of the powder bed. After addition of the semi-solid onto the powder bed or flattened powder, the whole material is compressed at 30kN into a single tablet, followed by ejection of the tablet. This results in a tablet with a semi-solid part embedded in the cleaning tablet. The density of the powdered region is 1.5 kg/litre, the density of the semi-solid part is 1.0 kg/litre. The height of the semi-solid part after compression is 3.4 mm, of the powdered part 11 mm.

Example III

[0097] Smooth cleaning tablet parts were made by the method of the previous examples. Each smooth part comprised:

Component parts by weight	Ref 25/7	Ref 50/16	Sample A1/A2	Sample B1/B2/B3
LAS-acid/Lutensol AO5[1] = 7/6	100	100	100	100
NaOH (50%), pH to ~11	13	13	13	13
Mono Propylene Glycol (MPG)	25	50	52.7	52.7
Pristerene 4916[2]	6.9	16. 3	14.5	14.5
NaOH (50%), pH to ~11	2	5	4.5	4.5
Co-surfactant	-	-	5	6.9

[1] Alkyl Benzene Sulphonic Acid/Ethoxylated fatty alcohol (C13-15E5) = 7/6 weight ratio

[2] C16-18 fatty acid

[0098] The selected co-surfactants were:

Trade name/description	Chemical description	Supplier	Used in example
Empicol CBC	Alkyl Ether Caboxylate, C12E4C	Huntsmann	A1
Empicol CBL	Alkyl Ether Caboxylate, C10-16E13C	Huntsmann	A2
Daclor 70-3-23-AL	Alkyl Ether Sulphate, C12-13E3S	Daclor	B1
Glucapon 600 CSUP	Alkyl PolyGlucoside, C10-16	Cognis	B2
C12-14 APG	Alkyl PolyGlucoside, C12-14G1.7	Cognis	B3
The co-surfactants used in examples A1, A2, B1, B2 and B3 were freeze dried untill water activities Aw<0.5 before incorporation into the mixture.			

[0099] The hardness of the Gels were quantified using Stevens LFRA Texture Analyser by measuring the resistance of a rod (diameter 12.7mm) pushed into the gel at a penetration speed of 1 mm/s at room temperature.

[0100] The dissolution rate was measured by measuring the time of dissolution of ~5 grams of smooth part in 1 liter of demineralised water under stirring at 200 rpm at 20C, the time was taken after 80% of the weight of the smooth sample was dissolved (T80).

Results

[0101]

Table 1

Hardness and Dissolution speed of the various Gels.		
Experiments	Stevens Hardness force (g)	Dissolution speed T80 (min)
Reference 25/7	10057	54
Reference 50/16	13069	47
Empicol CBC	11091	35
Empicol CBL	11422	32
LES(Daclor 70-3-23-AL)	11395	33
Glucopon 600 CSUP	10989	32
C12-14 APG	13425	29

Claims

1. A cleaning tablet comprising a smooth or semi-solid phase wherein the smooth or semi-solid phase comprises:

(a) from 10 to 90 wt% of non-soap surfactants; and
(b) from 2 to 75 wt% of soap;
(c) from 5 to 50 wt% a material selected from polyalkoxylated carbohydrates and stabilising surfactants having an average alkyl chain of more than 6 C atoms and having a salting out resistance greater than or equal to 3.0; and
(c) from 0 to 20 wt% of water.

2. A cleaning tablet according to claim 1, wherein the smooth or semi-solid phase has a weight of 2 to 20 grammes.

3. A cleaning tablet according to claim 1 comprising 3 to 70 wt % soap based on the weight of the smooth or semi-

solid phase.

4. A cleaning tablet comprising according to one or more of the preceding claims wherein the smooth phase is a semi-solid phase **characterised by** a ratio of F_f to E_b of less than 1.0,
F_f being the failure force
E_b being the break energy.

5. A cleaning tablet according to one or more of the preceding claims wherein the material is selected from the group of polyoxyethylene-sorbitan mono-fatty esters, polyoxyethylene-sorbitol fatty esters, polyoxyethylene glycerol esters, polyoxyethylene glyceril sorbitan isostearate, polyoxyethylene-hexitan-fatty esters, polyoxyethylene sorbitan, polyoxyethylene-sorbitol, polyoxyethylene glycerol, polyoxyethylene glycerol sorbitan, polypropoxylated sorbitan alkyl polyalkoxylated carboxylates, alkyl polyalkoxylated phosphates, alkyl polyalkoxylated sulphosuccinates, dialkyl diphenyl oxide disulphonates and alkyl polysaccharides or mixtures thereof.

6. A cleaning tablet according to claim 5, wherein the material is a polyethoxylated sorbitan or ester thereof.

7. A cleaning tablet according to claim 5 or 6, wherein the level of the material is from 10 to 45 wt% based on the weight of the smooth or semi-solid phase.

8. A cleaning tablet according to claim 1, wherein the material is a alkylpoly saccharide.

9. A cleaning tablet according to one or more of the preceding claims comprising 5 To 50 wt% of diluent, based on the weight of the smooth or semi-solid phase.

10. A cleaning tablet according to claim 8, wherein the diluent is dipropyleneglycol or mono propyleneglycol.

11. A cleaning tablet according to claim 1, wherein the stabilising surfactant has a salting out resistance greater or equal to 4.0 more preferred more than 5.0.

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number EP 03 07 7852

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A	WO 99 20730 A (UNILEVER PLC; UNILEVER NV) 29 April 1999 (1999-04-29) * example 4 *	1,3	
A	US 6 083 893 A (ZINT DAVID ROBERT ET AL) 4 July 2000 (2000-07-04) * example 1 *	1-3,9,10	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C11D

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 October 2003	Saunders, T

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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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

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European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 03 07 7852

Claim(s) searched completely:
2,3,5-10

Claim(s) searched incompletely:
1

Claim(s) not searched:
4,11

Reason for the limitation of the search:

Present claims 1, 4 and 11 relate to a product defined by reference to desirable characteristics or properties, namely the following :

P1: salting out resistance
P2: failure force/break energy ratio

The claims cover all products having these characteristics or properties, whereas the application provides support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 84 EPC). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for all of claims 2, 3 and 5-10, as well as for the parts of claim 1 which appear to be clear, supported and disclosed, namely cleaning tablets with a semi-solid phase comprising non-soap surfactants, soap and one or more of the polyalkoxylated carbohydrates or surfactants listed in claim 5 and one page 7, lines 1-24 of the description.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 07 7852

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27-10-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82