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(54) Detergent compositions

(57) Cleaning tablet comprising a soap rich phase, wherein said phase is obtained by compression of a particulate mixture comprising at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10 %wt, preferably at least 50% wt of soap surfactant. The tablet also comprises a second phase which is a solid phase of a compressed particulate composition.

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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 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.

[0005] A problem with multi-phase tablets is that often they may suffer from bleeding whereby ingredients from one phase of the tablet leek into the other phase. This may lead to undesirable effects such as degradation of ingredients or discoloration of the tablet. It is an object of the present invention to provide a method to produce a cleaning tablet comprising at least two phases, wherein said the tablet comprises surfactants and wherein said cleaning tablet has good dispersing properties and wherein the tablet does not suffer from unacceptable high degree of bleeding from one phase into the other phase(s).

A further objective of the present invention is to provide a method to produce a multi-phase tablet 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.

[0006] According to a first 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 soap rich region and at least one second region of the tablet is a solid region of compacted particulate material.

[0007] In a preferred aspect the invention also relates to a method for producing a cleaning tablet comprising a soap rich phase, wherein the production of the soap rich phase comprises the compression of a particulate composition comprising at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10 %wt, preferably at least 25% wt, more preferably at least 50% wt, of soap.

[0008] Preferably tablets of the invention are of cylindrical shape (e.g. round, rectangular or square) wherein the two main surfaces (upper side and bottom side) are substantially flat.

[0009] As indicated above, tablets of the invention are multiphase tablets wherein the soap rich phase is present and additionally one phase of compacted particulates is present. Suitably there may be additional phases to the compressed phase and the soap rich phase. In an especially advantageous embodiment of the invention the cleaning tablet further comprises at least one smooth phase. Most advantageous is the location of the soap rich phase as a barrier between the compressed phase and the smooth phase. Surprisingly it has been found that the soap rich layer significantly reduced the bleeding of ingredients from the smooth phase into the compressed phase, without unduly affecting the cleaning properties and dissolution properties of the cleaning tablet.

[0010] The regions of a multi-phase tablet are preferably separate layers within a cleaning 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 soap rich layer and the second region is a layer of compacted particulate material. In a further advantageous embodiment there is a third layer of smooth material, whereby the soap rich layer is located substantially as a barrier between the second and third layer.

[0011] If the tablet is a multi-phase tablet comprising the soap rich phase of the invention then preferably the soap rich phase is present as a distinctive region preferably having a weight of from 2 to 40 grammes, more preferred from 3 to 20 grammes, most preferred from 4 to 10 grammes. Preferably the other phases each have a weight of 2 to 40 grammes. Preferably the total weight of the cleaning tablet according to the invention is from 10 to 100 grammes, more preferred from 15 to 60 grammes, most preffered from 15 to 50 grammes.

[0012] For the purpose of the invention the term soap rich phase refers to a separate part of the tablet, e.g. a region, such as a layer, wherein the level of soap is at least 10% wt, more preferably at least 15% wt, still more preferably at least 20% wt, yet more preferably at least 25% wt. Typical soap levels in the soap rich phase are from 15% to 50% by weight, more preferably from 25% to 40% by weight. However, preferably the soap level is at least 50% wt and can even be very high say more than 80wt% or even more than 90 %wt up to 100 %wt based on the weight of the soap rich phase. Other ingredients may also be present in the soap rich layer, although preferably the soap rich layer is substantially free of non-soap surfactants, bleach ingredients and builder materials. Sometimes it may be advantageous however to incorporate into the soap rich layer a highly soluble material such as sugars, urea, alkali metal salts such as sodium chloride etc. Typically such highly soluble materials will have a solubility of at least 100 grammes per litre

water of 20 C, more preferred at least 250 grammes. Advantageously the level of these highly soluble materials in the soap rich phase is less than 50%wt, for example from 5 to 45 %wt, advantageously from 10 to 40 %wt.

[0013] The soap rich region of the tablet may be prepared by any suitable method for example the spraying, applying or brushing of a soap rich formulation, if appropriate followed by hardening e.g. by cooling. In a preferred method the soap rich layer is obtained from the compression of soap rich particles. Such detergent particles preferably comprise at least 10 %wt, more preferably at least 50%wt (based on the particles) of soap surfactants. Suitable detergent particles may for example be granules or other particles having high soap levels, for example soap noodles, marumes or granulates with high soap levels.

[0014] Preferably the level of soap surfactants in the soap rich particles is more than 50 %wt, more preferred more than 70 %wt, especially preferred from 75 %wt to 100 %wt. Preferably the level of soap rich particles in the soap rich phase is at least 60 wt%, more preferred from 80 to 100 wt%.

[0015] Further surfactants, for example anionic, nonionic or cationic surfactants may equally be present in the soap rich phase for example at a level of 0.1 to 10 %wt based on the weight of the soap rich part. However normally the first soap rich phase will be substantially free from non-soap surfactants.

[0016] In addition to the soap surfactants the soap rich region may comprise other materials for example soluble materials such as electrolyte materials, meltable organic materials and sugars, at a level of 2 to 70 %wt based on the weight of the smooth part, more preferred from 3 to 50 %wt, most preferred 5 to 40 wt%. Examples of preferred materials are water-soluble materials such as the sodium and potassium citrates, sodium chloride, acetates and carbonates, urea and sugar. The water solubility at 20 C of these materials is preferably at least 10 grammes per 100 ml of water, more preferred more than 15 grammes, most preferably more than 20 grammes.

[0017] If these soluble materials are present, their particle size is preferably chosen such that the soap rich phase is a soap rich continuous matrix having dispersed therein particles of the water soluble material.

[0018] It has been found that these materials provide good dissolution properties to the soap rich phase. Furthermore these materials do not negatively affect the desired firm consistency of the soap rich phase.

[0019] In a preferred embodiment of the intention the cleaning tablet comprises in addition to the soap rich phase and the compressed phase a smooth phase.

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

[0022] The smooth 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 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.

[0023] Preferably 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.

[0024] 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.

[0025] In an advantageous embodiment of the invention the smooth phase comprises from 30-100 %wt of non-soap surfactants, more preferred 40 to 90 %wt (based on the total weight of said smooth phase), more preferred from 50 to 80 %wt. It has been found that the combination of a separate smooth first region and these high non-soap surfactant levels provide very good dispersing and cleaning properties to the tablet.

[0026] Preferably the total weight of surfactants in the smooth phase is from 2 to 20 grammes, more preferred from 3 to 10 grammes.

[0027] In a first 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 non-soap surfactants. Especially the level of non-soap surfactants in the solid 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.

[0028] In a first embodiment of the invention the cleaning tablets comprise a first soap rich 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. Preferably cleaning tablets of the invention also comprise a third smooth region (as described above)

[0029] 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.

[0030] In a second preferred embodiment of the invention the cleaning tablets comprise a first soap rich region (as described above) in combination with a third smooth region. Such a third smooth region advantageously comprises 50-100 %wt of non-soap surfactants for examples 60 to 90 %wt in combination with optional ingredients such as to 0 to 50 wt% soluble materials (as described above) 0 to 40 wt% diluent materials (as described above) and 0 to 20 wt% (as described above) of water.

[0031] The non-soap surfactants in said third smooth phase may for example be anionic, nonionic or cationic non-soap surfactants or mixtures thereof. Relatively low levels of soap may also be present, for example up to 10 %wt based on said third smooth phase.

[0032] The above description of the tablet has been given with reference to a tablet constituted by two or three 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 soap rich region may be a single discrete part of the tablet but may also be a limited number (say 1-5) discrete soap rich parts. Preferably each of these soap rich parts are at least 2 grammes, also preferably each of these soap rich parts may be substantially of the same composition or of different 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 soap rich parts.

[0033] 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.

[0034] An especially preferred embodement of the invention relates to a multi-phase cleaning tablet comprising a soap rich first phase (as described above) in combination with a non-soap surfactant rich second smooth phase (as described above) and a solid region, for example as prepared by compression of a particulate compostion.

[0035] Preferably each of the regions in this preferred embodiment has a weight of 2 to 50 grammes. Preferably the soap rich phase is from 2 to 20 grammes for example 3 to 15 grammes. Preferably the non-soap surfactant rich phase is from 2 t 20 grammes, for example 3 to 15 grammes.

Preferably the solid phase is from 5 to 50 grammes, for example 10 to 40 grammes. Especially preferably the regions are present as layers in the cleaning tablet.

[0036] Cleaning tablets according to the invention are preferably manufactured by a process involving the application of pressure to a particulate mixture. Advantageously the preparation of the soap rich phase may involve the dosing of a particulate mixure comprising soap rich particles optionally in combination with other materials as described above, followed by the exertion of pressure, preferably above the yield stress of the soap rich particles. It has been found that the exertion of pressure to a particulate mixture comprising significant levels of soap rich particles leads to a certain flow behaviour of the mixture leading to the formation of a continuous, soap rich phase.

[0037] Although applicants do not wish to be bound by any theory it is believed that the advantageous process of the invention works as follows: Typically compaction of soft solid leads to a decrease in inter-particle porosity relative to a particle bed simply due to reduced air entrainment. However at a certain compaction force (yield stress) the individual particles will deform and flow into the interparticle voids leading to a semi-continuous network of intermeshed particles with no or low porosity and a smooth appearance.

[0038] Detergent particles for use in the preparation of the soap rich phase preferably have a relatively high soap level of at least 10% wt, more preferred more than 50 %wt, yet more preferred more than 55 %wt, most preferred from 60 to 90 or even 100 %wt.

[0039] A multi-phase tablet comprising a soap rich phase may advantageously be made by a process, comprising the steps of:

(a) inserting a first particulate composition into a tablet mould

(b) inserting a second particulate composition into said tablet mould, wherein said second particulate composition comprises at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10 %wt, preferably at least 25%wt, more preferably at least 50%wt, of soap surfactants;

(c) compression of the particulate compositions to form a compressed tablet comprising discrete regions, wherein the first region is formed by said compressed first composition and the second region is formed by said compressed second composition.

[0040] Preferably step (a) takes place before step (b). Preferably the first particulate composition is such that upon compression a solid phase of compressed particulate material is formed.

[0041] In a preferred embodiment of the invention the first particulate composition is pre-compressed at a force of 0.1 to 20 kN/cm^2 between steps (a) and (b). In another preferred embodiment, the particulate composition is flattened between steps (a) and (b).

[0042] Preferably the (co-) compression of the combination of the soap rich and the solid region(s) takes place at a force of from 0.05 to 20 kN/cm^2. Especially if the solid region has been pre-compressed the co-compression in step (c) can advantageously be at a force of 0.1- 10 kN/cm^2, more preferred 0.5 to 5 kN/cm^2. If the solid region has not been pre-compressed, the co-compression preferably takes place at a force of 1- 100 kN/cm^2., more preferred 2-50 kN/cm^2., most preferred 2-10 kN/cm^2.

[0043] If the tablet of the invention comprises a soap-rich phase as described above this phase may also be manufactured seperately by compression of a particulate soap rich material e.g. at the compation forces as indicated above.

[0044] Alternatively the soap rich phase may be prepared by other methods for example the spraying of a soap rich composition for example onto the (pre) compressed compacted tablet phase. Another suitable method for the preparation of a soap rich phase may involve casting or extrusion of a soap rich composition.

[0045] Optionally the smooth (preferably non-soap surfactant) phase may also be prepared e.g. by extrusion, casting or other shaping methods.

[0046] Seperately prepared soap rich phase and non-soap surfactant rich phase can then be adhered to other parts of the tablet for example by gentle pressing or by usage of an adhesive material.

[0047] Similarly a seperately prepared solid phase e.g. of compressed particulate meterials can be combined with one ore more pre-prepared soap rich phases e.g. by gentle co-compression.

[0048] A tablet of this invention may be intended for use in machine dishwashing. Such tablets will typically contain salts, such as over 60 wt% of the tablet.

[0049] 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.

[0050] 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% soap surfactant based on the whole tablet, and from 5 to 80 wt% detergency builder, based on the whole tablet.

[0051] Materials which may be used in tablets of this invention will now be discussed in more detail.

Surfactant Compounds

[0052] 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 soap), cationic, zwitterionic, amphoteric, nonionic or a combination of these.

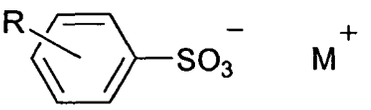
[0053] Anionic surfactant may be present in an amount from 0.5 to 50% by weight, preferably from 2% or 4% up to 30% or 40% by weight of the tablet composition.

[0054] 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.

[0055] 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.

[0056] 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 soap surfactant in the composition.

[0057] 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.

[0058] Soaps for use in accordance to the invention are preferably alkali metal or alkaline earth metal salts of naturally occuring fatty acids, 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.

[0059] 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.

[0060] 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.

[0061] 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.

[0062] 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.

[0063] Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition.

[0064] In a machine dishwashing tablet the surfactant may be wholy 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

[0065] 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.

[0066] 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:

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

[0067] 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.

[0068] 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.

[0069] 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 $NaMSi_xO_{2x+1}{\cdot}yH_2O$ 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.

[0070] 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.

[0071] 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, carboxymethyloxy-

malonates, dipicolinates and hydroxyethyliminodiacetates.

[0072] 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

[0073] 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.

[0074] 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.

[0075] 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

[0076] 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.

[0077] 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.

[0078] 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.

[0079] 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.

[0080] 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.

[0081] 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.

[0082] 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

[0083] The first soap rich region of the cleaning tablet may advantageoulsy be prepared by compacting particles with a high soap content as described above. Preferably these particles have a mean particle size of from 100 to 1000 μm.

[0084] The second region of a detergent tablet of this invention, is a preferably a matrix of compacted particles.

[0085] Preferably the particulate composition has a mean 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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.

[0091] The present invention will now be explained in more detail by way of the following non-limiting examples.

Example 1

[0092] A first particulate composition was prepared as follows. A 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	
Linear alkylbenzene sulphonate, sodium salt	4.2
Alcohol ethoxylate nonionic, avg. 7EO	1.8
C16-18 soap	0.3
Zeolite A24	9.3
Sodium acetate, 3aq.	1.2
Sodium carbonate	1.4
Sodium carboxymethyl cellulose	0.1
Moisture, salts	balance
Post-dose	
Antifoam adjunct	1.0
Fluorescer adjunct	2.3
Sodium tripolyphosphate	48.0
Sodium silicate	2.5
Tetraacetyldiethylenediamine(TAED)	4.5
Sodium percarbonate	17.2
Ethylene diamine tetra(methylene	

(continued)

Ingredient	*Parts by weight*
Post-dose	
phosphonate)	2.7
Minors (perfume,enzymes)	1.7

Solid phase preparation:

[0093] 20 grammes of the of the first particulate composition are inserted into a 45 mm die of a tabletting machine, optionally followed by a flattening step. The whole material is compressed at 30kN into a single tablet.

Soap rich phase preparation:

[0094] 5 grammes of C12-C14 soap particles were dosed in the tablet mould on top of the solid phase, followed by a second compression step of 10 kN resulting in the formation of a first soap rich phase on top of the solid phase.

Non-soap surfactant rich smooth phase preparation:

[0095] This smooth phase was prepared of the following composition:

Ingredient	*Parts by weight*
Na-las	39.1
Nonionic 7EO	33.5
C12 soap	7.3
Monopropyleenglycol	to 100

[0096] The mixture was heated to 80°C and casted into moulds and cooled to 20°C to form firm, 5 grammes smooth, semi-solid parts of 45mm diameter.

[0097] A smooth part is then applied to the top of the tablet e.g. by gentle compression. The resulting tablet is a three-layer tablet whereby the soap-rich layer is located between the solid phase and the smooth phase.

Examples 2, 3, A

[0098] The compressed particulate phase had the following composition:

Composition (%wt)	P1
Na-LAS	4.15
Nonionic 7EO	1.82
Soap	0.33
zeolite A24 (anhydrous)	9.30
Na Acetate.3aq	1.18
Na Carbonate	1.38
SCMC (68%)	0.18
Moisture, salts, NDOM	1.67
Antifoam granule	1.01
Fluorescer granule (15 % active)	2.31
STP HPA	48.1
Nabion/Disilicate co granule.	2.50

(continued)

Composition (%wt)	P1
TAED (as gran.83%)	4.52
Coated Percarbonate	17.2
Dequest 2047 (43%)	2.70
Enzymes	0.94
Perfume	0.71
TOTAL	100.0

[0099] The following compositions were used for the intermediate phase:

Composition (%wt)	I1	I2
Soap granules (Prisavon 1878 ex Uniqema)	25	50
Granular sodium sulphate	75	50

[0100] The semi-solid phase had the following composition:

Composition (%wt)	S1
Na-LAS	32.90
Nonionic 5EO	27.35
Na soap (C16/C18)	2.96
Tween 40	12.05
DiPropyleneGlycol	17.77
Dye	0.011
Water	6.96
Total	100

[0101] In Example 2, a tablet consisting of a compressed particulate phase, an intermediate phase and a semi-solid phase was produced by first compressing 25 gr of composition P1 in a Fette tabletting machine. An intermediate phase was then formed on top of this particulate phase, by compressing 2 gr of composition I1 in the same Fette tabletting machine.

The semi-solid phase was produced by casting 5 gr of liquid composition S1 at 90°C into a mould, after which the phase was let to solidify. The semi-solid phase was then glued onto the intermediate phase with 0.3 gr of a hot melt water-soluble glue, to form the complete tablet.

[0102] To demonstrate the necessity of the intermediate phase, tablets were made in the same manner as in Example 2, but now using composition 12 for the intermediate layer (Example 3) and a tablet which did not contain an intermediate layer (comparative Example A).

[0103] The full tablets thus made were flow wrapped and packed in carton boxes and stored for 7 weeks at 37°C and 70% relative humidity.

After the storage period, the semi-solid phases were carefully removed and re-weighed. The loss in weight (in % of the original gel weight) is a measure of the amount leaked into the compacted particulate phase. The compacted particulate phase was examined visually for changes in colour.

The table below shows the results:

Example	2	3	A
Weight loss of gel (%wt)	4	6	28
Colour of compacted particulate phase	white	white	Yellow spots

[0104] This result clearly shows the necessity of the intermediate layer to provide stability upon storage, which is an essential feature for these tablets. It also shows that even at fairly low levels of soap (Example 2) surprisingly good barrier properties can be obtained.

Claims

1. A method for producing a cleaning tablet comprising a soap rich phase, comprising the compression of a particulate composition comprising at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10 %wt, preferably at least 25%wt, more preferably at least 50 %wt of soap surfactants.

2. A method according to claim 1 comprising the steps of

(a) inserting a first particulate composition into a tablet mould
(b) inserting a second particulate composition into said tablet mould, wherein said second particulate composition comprises at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10% wt, preferably at least 50 %wt of soap surfactants;
(c) compression of the particulate compositions to form a compressed tablet comprising discrete regions, wherein the first region is formed by said compressed first composition and the second region is formed by said compressed second composition.

3. A method according to claim 2 wherein step (a) takes place before step (b).

4. A method according to claim 2 wherein the (co-) compression of the combination of the smooth and the solid region(s) takes place at a force of from 0.05 to 20 kN/cm^2.

5. Cleaning tablet comprising a soap rich phase, wherein said soap rich phase is obtained by compression of a particulate mixture comprising at least 50 %wt of detergent particles, wherein said detergent particles comprise at least 10% wt, preferably at least 50 %wt of soap surfactant, and a second phase, which is a solid phase of a compressed particulate composition.

6. Cleaning tablet according to claim 5, further comprising a smooth phase comprising at least 50 %wt (based on the weight of said phase) of non-soap surfactants.

7. Cleaning tablet comprising a first soap rich phase comprising at least 10%wt, preferably at least 25% wt (based on said phase) of soap, a second smooth, phase comprising from 50 to 100 %wt (based on said phase) of non-soap surfactants and a third, solid phase of compressed particulate material.

8. Cleaning tablet according to claim 7, wherein each of the phases has a weight of from 2 to 40 grammes.

10. Cleaning tablet according to claim 8, wherein the first soap rich phase is located as a layer between the smooth phase and the solid phase.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 07 7426

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)
A	WO 99/41353 A (UNILEVER PLC ; GORDON JAMES WILLIAM (GB); LEVER HINDUSTAN LTD (IN); LE) 19 August 1999 (1999-08-19) * example 2 * -----	1-10	C11D17/00 C11D10/04 C11D11/00
A	WO 01/29162 A (HENKEL KGAA) 26 April 2001 (2001-04-26) * examples * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	17 September 2004	Saunders, T

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 07 7426

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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17-09-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9941353 A	19-08-1999	AU 746331 B2	18-04-2002
		AU 2520999 A	30-08-1999
		AU 2522099 A	30-08-1999
		BR 9907807 A	17-10-2000
		BR 9907811 A	17-10-2000
		CA 2318065 A1	19-08-1999
		CA 2318067 A1	19-08-1999
		CN 1290294 T	04-04-2001
		CN 1290295 T	04-04-2001
		CZ 20002935 A3	17-10-2001
		CZ 20002936 A3	14-11-2001
		DE 69914457 D1	04-03-2004
		DE 69914582 D1	11-03-2004
		DE 69914582 T2	05-08-2004
		WO 9941352 A1	19-08-1999
		WO 9941353 A1	19-08-1999
		EP 1054946 A1	29-11-2000
		EP 1054947 A1	29-11-2000
		HU 0100685 A2	28-06-2001
		HU 0101059 A2	28-08-2001
		PL 342193 A1	21-05-2001
		PL 342240 A1	04-06-2001
		TR 200002330 T2	21-12-2000
		TR 200002331 T2	23-07-2001
		US 6066615 A	23-05-2000
		US 6534473 B1	18-03-2003
		ZA 9901027 A	09-10-2000
		ZA 9901057 A	10-08-2000
WO 0129162 A	26-04-2001	DE 19950765 A1	26-04-2001
		AU 7787000 A	30-04-2001
		CA 2324070 A1	21-04-2001
		WO 0129162 A1	26-04-2001

EPO FORM P0459

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