

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 239 029 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
31.08.2005 Bulletin 2005/35

(51) Int Cl.7: **C11D 17/00**

(21) Application number: **01301982.3**

(22) Date of filing: **05.03.2001**

(54) **Cleaning compositions**

Wasch- oder Reinigungsmittel

Compositions de nettoyage

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(43) Date of publication of application:
11.09.2002 Bulletin 2002/37

(73) Proprietors:
• **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB IE
• **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GR IT LI LU MC NL
PT SE TR**

(72) Inventors:
• **Euser, Huug,**
c/o Lever Faberge Europe-Dev. Centre
3133 AT Vlaardingen (NL)
• **Tomlinson, Alan Digby,**
c/o Lever Faberge Europe
van Noortlaan 120, 3133 AT Vlaardingen (NL)

(74) Representative: **Boerma, Caroline et al**
Unilever N.V.
Unilever Intellectual Property Group
Olivier van Noortlaan 120
3133 AT Vlaardingen (NL)

(56) References cited:
EP-A- 0 481 547 EP-A- 0 522 766
EP-A- 0 711 827 WO-A-99/27063
DE-A- 19 918 458 DE-A- 19 957 504

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 239 029 B1

Description

[0001] This invention relates to cleaning compositions in the form of shaped bodies, usually referred to as tablets, intended to dissolve and/or disintegrate and so be consumed completely when placed in water at the time of use.

[0002] The tablets may be formulated for use in washing fabrics, or in washing dishes and other culinary utensils (collectively referred to as "ware"). A tablet may provide the whole composition which is to be used, or may be an additive which supplements another composition. The tablets may be used in an automatic washing machine or dishwasher. However, the invention could also be applied to other kinds of cleaning compositions in tablet form such as tablets intended to be added to water to provide wash liquors for use in hard surface cleaning, or in hand washing of fabrics or ware.

[0003] The invention is concerned with tablets made at least in part by compaction of a particulate composition. Such tablets are known, and marketed commercially. A number of consumers prefer tablets to powder products because they do not require measuring and are (usually) more compact so that less storage space is required.

[0004] Detergent compositions in tablet form and intended for fabric washing have been described in a number of patent documents including, for example, EP-A-711827, WO-98/42817 and WO-99/20730 (Unilever). Tablets of composition suitable for machine dish washing have been disclosed in EP-A-318204 and US-A-5691293. It is desirable that tablets have adequate strength when dry, yet disperse and dissolve within a required time when added to water at the time of use.

[0005] In the case of tablets for machine dish washing it may be desirable to formulate the tablets to remain intact during a pre-wash cycle, and then dissolve during a main-wash cycle.

[0006] In the case of tablets for use in laundering of fabrics, it is usually desirable to formulate the tablets to dissolve rapidly when they come into contact with water.

[0007] Known tablets made by the compaction of particulate mixtures are porous and generally have a matte surface which may be white or coloured. It is known to apply a coating material to the surface of tablets in a separate manufacturing operation after compaction. Such a coating may be a film-forming material serving to reduce the friability of the tablet surface and/or enhance tablet strength.

[0008] It is known to incorporate relatively low-melting materials, other than organic surfactants, into detergent tablets to act as binders. More specifically, it is known to incorporate a small percentage, such as 3 to 5% by weight, of a polyethylene glycol with a melting point below 80°C. This is exemplified in EP-522766 and EP 711828 (Unilever). These small percentages of binder increase the strength of tablets and may well allow compaction pressures to be reduced. The tablets have a matte surface similar to that of tablets made without such binder.

[0009] EP 481 547 discloses machine dishwashing tablets having a plurality of layers and comprising copolymers within a barrier layer surrounded by an outer layer.

[0010] DE 199 18 458 discloses processing liquid enzyme preparations with coating materials such as polyethylene glycols into melt dispersions which are introduced into or onto a tablet.

[0011] DE 199 57 504 discloses stable non-separating melts in which meltable materials such as paraffin wax or polyalkylene glycols are combined with fatty material, surfactant and other actives.

[0012] WO 99 27063 discloses a compressed tablet comprising a coating layer of polyethylene glycol.

[0013] The present invention provides a three-layer tablet, of cleaning composition in which a discrete region of the tablet, providing at least part of the tablet exterior, is a compacted particulate composition containing at least 10% by weight of the composition of the region, of water-soluble material, plastically deformable under pressure and melting at a temperature in a range from 30° to 90°C, wherein solid particulate material which is mixed with the plastically deformable material has an average particle size of 500 micrometers or less, and wherein the discrete region is the middle layer of the three layers.

[0014] Usually each region is derived by compaction from a respective particulate composition. In a heterogeneous body according to the present invention, the water-soluble material which confers a smooth or glossy surface is present in a region which is visible at the exterior of the tablet. Preferably, each discrete region has a mass of at least 2gm.

[0015] The invention is utilised for the middle layer of a tablet with three layers. This middle layer is then visually distinct from the other two layers. A further advantage is that the meltable material acts as a binder, and promotes adhesion of the two outer layers to the middle layer.

[0016] A tablet in accordance with this invention may have a variety of shapes. One simple shape is a cylindrical tablet, which may be divided into a plurality of layers each of which is a thinner cylinder of the same diameter and on the same axis. Tablets may have other cross sectional shapes (for example square or rectangular, with rounded corners) but generally a stack of layers, all of the same cross section, is preferred. The invention could, however, be embodied as tablets of other shapes, if desired.

[0017] In another aspect this invention provides a method of making a three-layer tablet, as defined above by compacting a particulate composition containing at least 10% by weight of the composition of water-soluble material which is plastically deformable under pressure and melting at a temperature in a range from 30° to 90°C.

[0018] Preferably the method includes a preceding step of mixing the said material with other particulate material, in proportions between 10:90 and 99:1 by weight. The proportions may lie in a range from 15:85 up to 95:5 or 99:1.

[0019] When making a tablet with a plurality of layers, particulate material for each of the layers is successively introduced into a mould. Generally a so-called precompaction (i.e. a light compaction pressure) is applied to the contents of the mould after adding the material for each layer, except the last layer. After material for the last layer is added to the mould and compaction pressure is applied to the entire content of the mould to form the tablet.

[0020] A region of a tablet which embodies this invention may possibly contain some organic surfactant. However, it is preferred that the amount of the said plastically deformable material which melts between 30° and 90°C is greater than the total amount of the following organic surfactants, (if present).

- anionic surfactants containing a hydrophobic alkyl, alkenyl or alkyl-aryl group of at least 8 carbon atoms, connected to a sulphate, sulphonate or carbonate hydrophilic group
- nonionic surfactants containing a hydrophobic alkyl, alkenyl or alkyl-aryl group of at least 8 carbon atoms, connected to a poly (alkylene oxide) chain containing an average of 15 alkylene oxide residues or less.

[0021] Such surfactants are apt to be slow to dissolve from compositions in tablet form, because they form viscous gel phases as they start to take up water. In consequence they can inhibit the dissolution/disintegration of a tablet when placed in water.

[0022] It is desirable that the above organic surfactant provide no more than 18%, better no more than 9% of the composition of the tablet region or homogenous tablet in accordance with this invention.

[0023] Nonionic surfactants with an average of 20 or more, better 40 or more ethylene oxide residues may possibly be incorporated in a region of a tablet (or a homogenous tablet) which contains plastically deformable material in accordance with this invention.

[0024] An example of such a material is Lutensol 80 from BASF which is C₁₆/C₁₈ fatty alcohol ethoxylated with an average of 80 ethylene oxide residues.

[0025] A region of a tablet in accordance with this invention will usually contain some particulate material which is neither an organic surfactant nor the water-soluble plastically deformable material which melts between 30° and 90°C. This other particulate material may be water-insoluble, such as zeolite builder particles or it may be one or more water-soluble salts, such as peroxygen bleach, sodium citrate or sodium tripolyphosphate builder.

[0026] If the plastically deformable material is used alone, or without much particulate solid, it can have a translucent appearance as well as a glossy surface. Incorporation of solid particulate material tends to reduce translucency, if the particle size is large. Solid particulate material which is mixed with the plastically deformable material has an average particle size of 500 micrometers or less, better an average particle size not exceeding 400 or even 300 micrometers. This promotes a translucent appearance of the compacted tablet region or tablet, as well as a glossy surface finish.

[0027] Preferred forms of this invention use a material which contains polyoxyethylene chains. Consequently, in a preferred aspect, this invention provides a tablet of cleaning composition in which the tablet or a discrete region of the tablet is a compacted particulate composition containing at least 10% by weight of the composition, of water-soluble material melting at a temperature in a range from 30° to 90°C, and which is an organic material containing a polyoxyethylene chain in which there is an average of at least 20 ethylene oxide residues.

[0028] In another preferred aspect the invention provides a method of making a three-layer tablet as defined above characterised by compacting a particulate composition containing at least 10% by weight of water-soluble material melting at a temperature in a range from 30° to 90°C, and which is an organic material containing a polyoxyethylene chain in which there is an average of at least 20 ethylene oxide residues.

[0029] A tablet of this invention is likely to contain one or more of organic surfactant, detergency builder and bleach. Tablets for fabric washing will normally contain overall more organic surfactant than tablets for machine dish washing. Tablets intended to be used as an additive may contain bleach as their main or only active ingredient.

[0030] Materials which may be used in compositions embodying this invention will now be discussed by turn.

The Plastically Deformable and Meltable Binder Material

[0031] This material must be capable of existing in a particulate form in the composition which is compacted into a shaped body or region thereof. It will therefore be solid, either amorphous or crystalline, at ambient temperatures of 15 to 25°C and preferably somewhat above.

[0032] This material must be such that its particles can merge together when subjected to the compaction pressure. This is characteristic of plastically deformable materials which soften at temperatures which are not too much above ambient.

[0033] A softening or melting temperature above ambient, desirably at least 35°C is desirable, better at least 40°C depending on where the tablets will be sold and used. Preferably the melting temperature does not exceed 80°C, or

even 70°C, since a lower melting temperature facilitates fusion of the particles of the material during compaction.

[0034] This material should be water-soluble. A solubility of at least 10gm per 100gm deionised water at 20°C is desirable. Higher solubilities, such as at least 20gm per 100 gm, are preferred.

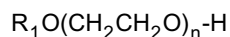
[0035] Preferred materials are organic polymers containing polar groups, especially polyethylene glycol (PEG). Polyethylene glycols of molecular weight from 1500 to 10,000 and above have been found suitable, especially those of molecular weight in a range from 3000 to 8000.

[0036] Other plastically deformable organic polymers with a high proportion of hydrophilic groups could be employed. Possibilities are polyacrylates and polyvinyl pyrrolidone.

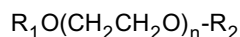
[0037] The material may have surfactant properties provided it includes a high proportion of polar groups. Possibilities include nonionic surfactants containing an average of 20 or more (preferably 30 or more) ethylene oxide residues, for example polyoxyethylene monostearates with average 20, 40, 75 or more ethylene oxide residues, and polyoxyethylene lauryl ethers with average 23 or more ethylene oxide residues.

[0038] Compounds with a polyoxyethylene chain terminated at one end by some other group can also be categorised as mono-capped ethylene glycols.

[0039] The plastically deformable material may be a mono-capped polyethylene glycol of the formula



or a di-capped polyethylene glycol of the formula



in which n is at least 20 and R_1 and R_2 are, independently of each other, substituted or unsubstituted hydrocarbon groups containing from 1 up to 20 or 30 carbon atoms, provided the material has a melting temperature somewhere in the range from 30° to 90°C.

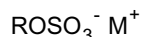
Surfactant Compounds

[0040] Compositions which are compacted to form tablets or regions of tablet may contain one or more organic 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. Anionic surfactant may be present in fabric washing tablets in an amount from 0.5 to 50% by weight, preferably from 4% up to 30% or 40% by weight of the tablet composition. It may be accompanied by nonionic surfactant in an amount from 3% to 20% by weight of the composition.

[0041] In a machine dishwashing composition, organic surfactant is likely to constitute from 0.5 to 8%, more likely from 0.5 to 6% of the overall composition and is likely to consist of nonionic surfactant, either alone or in a mixture with anionic surfactant.

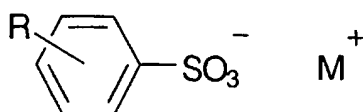
[0042] Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8 - C_{15} ; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0043] Primary alkyl sulphate having the formula



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

[0044] 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.

[0045] 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.

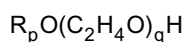
[0046] In some forms of this invention the amount of non-soap anionic surfactant lies in a range from 5 to 20 or 25 wt% of the tablet composition.

[0047] It may also be desirable to include one or more soaps of fatty acids. These 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.

[0048] 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.

[0049] Specific nonionic surfactant compounds are alkyl (C₈₋₂₂) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic C₈₋₂₀ 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.

[0050] Especially preferred are the primary and secondary alcohol ethoxylates, especially the C₉₋₁₁ and C₁₂₋₁₅ primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol. It is desirable that alkoxylation is carried out with ethylene oxide only, so that the resulting mixture of compounds complies with a general formula

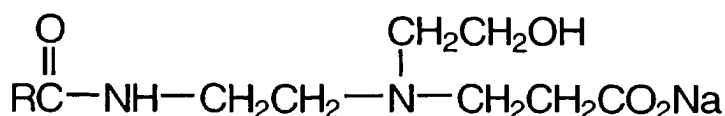


where p has a mean value of 6 to 15 and q has a mean value of 5 to 20, preferably 5 to 9.

[0051] Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition, prior to compaction into tablets.

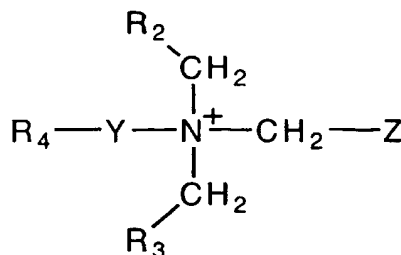
[0052] Preferred nonionic surfactants for use in machine dishwashing tablets are low to non-foaming nonionic surfactants containing ethylene oxide and/or propylene oxide residues. Examples of suitable low to non-foaming ethoxylated straight-chain alcohols which are preferred nonionic surfactants in machine dishwashing are the Plurafac LF series ex BASF, the Synperonic series ex ICI; the Lutensol® LF series, ex BASF, and the Triton® DF series, ex Rohm & Haas. Also of interest are the endcapped ethoxylated alcohols available as the SLF 18B series from Olin.

[0053] Amphoteric surfactants which may be used jointly with anionic or nonionic surfactants or both, notably in fabric washing formulations include amphopropionates of the formula:



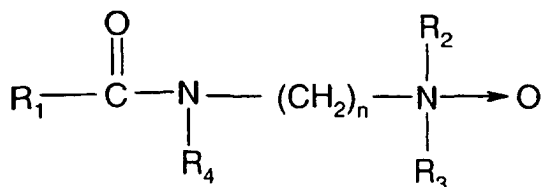
where RCO is a acyl group of 8 to 18 carbon atoms, especially coconut acyl.

[0054] The category of amphoteric surfactants also includes amine oxides and also zwitterionic surfactants, notably betaines of the general formula



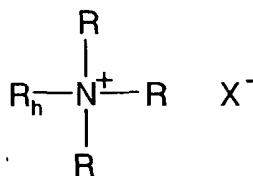
where R_4 is an aliphatic hydrocarbon chain which contains 7 to 17 carbon atoms, R_2 and R_3 are independently hydrogen, alkyl of 1 to 4 carbon atoms or hydroxyalkyl of 1 to 4 carbon atoms such as CH_2OH , Y is CH_2 or of the form $\text{CONHCH}_2\text{CH}_2\text{CH}_2$ (amidopropyl betaine); Z is either a COO^- (carboxybetaine), or of the form $\text{CHOHCH}_2\text{SO}_3^-$ (sulfobetaine or hydroxy sultaine).

[0055] Another example of amphoteric surfactant is amine oxide of the formula



where R_1 is C_{10} to C_{20} alkyl or alkenyl; R_2 , R_3 and R_4 are each hydrogen or C_1 to C_4 alkyl, while n is from 1 to 5.

[0056] Cationic surfactants may possibly be used. These frequently have a quaternised nitrogen atom in a polar head group and an attached hydrocarbon group of sufficient length to be hydrophobic. A general formula for one category of cationic surfactants is



where each R independently denotes an alkyl group or hydroxyalkyl group of 1 to 3 carbon atoms and R_h denotes an aromatic, aliphatic or mixed aromatic and aliphatic group of 6 to 24 carbon atoms, preferably an alkyl or alkenyl group of 8 to 22 carbon atoms and X^- is a counterion.

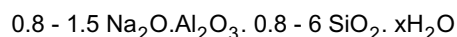
[0057] The amount of amphoteric surfactant, if any, may possibly be from 3% to 20 or 30% by weight of the tablet or region of a tablet; the amount of cationic surfactant, if any, may possibly be from 1% to 10 or 20% by weight of the tablet or region of a tablet.

Detergency Builders

[0058] A composition which is compacted to form tablets or tablet regions may contain a so-called builder which serves to remove or sequester calcium and/or magnesium ions in the water.

[0059] When a water-softening detergency builder is present, the amount of it is likely to lie in a broad range from 5 better 15 wt% up to 80% of the tablet composition.

[0060] Alkali metal aluminosilicates are strongly favoured as environmentally acceptable water-insoluble detergency builders. Alkali metal (preferably sodium) aluminosilicates may be either crystalline or amorphous or mixtures thereof, having the general formula:



[0061] These materials contain some bound water (indicated as $x\text{H}_2\text{O}$) and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g . The preferred sodium aluminosilicates contain 1.5-3.5 SiO_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.

[0062] Suitable crystalline sodium aluminosilicate ionexchange materials 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 newer zeolite P described and claimed in EP 384070 (Unilever) and mixtures thereof. This form of zeolite P is also referred to as "zeolite MAP". One commercial form of it is denoted "zeolite A24".

[0063] Conceivably a detergency builder of poor water solubility 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 $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used.

[0064] Non-phosphorus water-soluble water-softening builders may be organic or inorganic. Inorganics that may be present include alkali metal (generally sodium) carbonate; while organics 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, nitrilotriacetates and hydroxyethyliminodiacetates.

[0065] Tablet compositions preferably include polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers which have some function as water-softening agents and also inhibit unwanted deposition onto fabric from a laundry wash liquor or onto glass from a machine dish wash liquor.

[0066] The category of water-soluble phosphorus-containing inorganic builders includes the alkali-metal orthophosphates, metaphosphates, pyrophosphates and polyphosphates. Specific examples of inorganic phosphate detergency builders include sodium and potassium tripolyphosphates, orthophosphates and hexametaphosphates.

[0067] Sodium tripolyphosphate may be incorporated in hydrated, anhydrous or partially hydrated form. It has been found advantageous to employ sodium tripolyphosphate which is rich in the phase I anhydrous crystalline form, as disclosed in EP-A-839906 (Unilever). As explained in that document, sodium tripolyphosphate can be converted to the phase I form by heating to above the transition temperature at which phase II anhydrous sodium polyphosphonate is transformed into the phase I form. A process for the manufacture of particles containing a high proportion of the phase I form of sodium tripolyphosphate by spray drying below 420°C is given in US-A-4536377.

[0068] This sodium tripolyphosphate is preferably partially hydrated, but the phase I anhydrous form should also be present. Thus, sodium tripolyphosphate particles may incorporate up to 5% (by weight of the sodium tripolyphosphate in these particles) of water of hydration. The extent of hydration is desirably from 1% to 4% or 5% by weight. Suitable material is commercially available. Suppliers include Rhodia, Courbevoie, France and Albright & Wilson, Warley, West Midlands, UK.

[0069] The sodium tripolyphosphate in these particles is preferably hydrated by a process which leads to a homogeneous distribution of the water of hydration within the tripolyphosphate.

[0070] This can be accomplished by exposing anhydrous sodium tripolyphosphate to steam or moist air. The particles preferably consist solely of sodium tripolyphosphate with a high content of the phase I form. The phase I content of the sodium tripolyphosphate being measured by X-ray diffraction, or IR.

[0071] The particles preferably contain sodium tripolyphosphate in a porous form so as to have high surface area. This can be achieved by spray drying the tripolyphosphate as a mixture with a blowing agent, that is a compound such as ammonium carbonate which decomposes to yield a gas during the course of the spray drying. This gives the dried material a porous structure, with higher surface area than hollow beads of tripolyphosphate obtained without blowing agent.

[0072] The bulk density of the of sodium tripolyphosphate particles is preferably 0.75 Kg/M^3 or less, more preferably from 0.52 to 0.72 Kg/M^3 .

[0073] The particles which contain or consist of sodium tripolyphosphate preferably have a small mean particle size, such as not over $300\mu\text{m}$, better not over $250\mu\text{m}$. Small particle size can if necessary be achieved by grinding.

[0074] Uniform prehydration, high phase I content, porosity and small particle size all promote rapid hydration when the tripolyphosphate comes into contact with water. A standard test for the rapidity of hydration is the Olten test. It is desirable that in such a test the tripolyphosphate reaches 90% of the final value (i.e. 90% of complete hydration when exposed to water at 80°C) within 60 seconds.

[0075] "Rhodiaphos HPA 3.5" is a grade of sodium tripolyphosphate from Rhodia which has been found to be particularly suitable. It consists of porous particles of small particle size (mean size below $250\mu\text{m}$) with 70% phase I and prehydrated with 3.5% water of hydration.

[0076] This form of sodium tripolyphosphate, with its small particle size, is a preferred type of sodium tripolyphosphate for incorporation into a tablet region in accordance with the invention, together with the said fusible and water-soluble material which confers the glossy surface.

[0077] Another region of a tablet may also incorporate this form of sodium tripolyphosphate, alone or jointly with some other form. A mixture of two forms of sodium tripolyphosphate may be used to regulate the speed of tablet disintegration/dissolution, especially in machine dishwashing tablets.

Silicates

[0078] Alkali metal silicates may be included. Amorphous silicas which will dissolve in an alkaline wash liquor may

be included in machine dish wash formulations. These may provide pH adjusting capability and protection against corrosion of metals (including washing machine parts) and against attack on dishware, including fine china and glassware benefits. If silicates are present, they are preferably included at a level of from 1% to 30%, preferably from 2% to 20%, more preferably from 3% to 10%, based on the weight of the composition. The ratio of SiO_2 to the alkali metal oxide (M_2O , where M = alkali metal) is typically from 1 to 3.5, preferably from 1.6 to 3, more preferably from 2 to 2.8.

Preferably, the alkali metal silicate is hydrous, having from 15% to 25% water, more preferably, from 17% to 20%.
[0079] The highly alkali metasilicates can in general be employed, although the less alkaline hydrous alkali metal silicates having a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from 2.0 to 2.4 are preferred. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles have a mean particle size between 400 and 700 micrometers.

Bleach System

[0080] Tableted compositions according to the invention may contain a bleach system. 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 85% by weight of the composition. If the tablet contains surfactant and detergency builder, the amount of peroxygen compound bleach is unlikely to exceed 25% of the composition.

[0081] Organic monoperoxy acids include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring-substituted peroxybenzoic acids (e.g. peroxy- α -naphthoic acid); aliphatic and substituted aliphatic monoperoxy acids (e.g. peroxyauric acid and peroxysebacic acid); and phthaloyl amido peroxy caproic acid (PAP). Organic diperoxy acids include alkyl diperoxy acids and aryldiperoxy acids, such as 1,12-diperoxy-dodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxy isophthalic acid; and 2-decyldiperoxybutane-1,4-dioic acid.

[0082] Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. Monopersulphate is a further possibility.

[0083] Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylene 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.

[0084] Chlorine bleaches may be used, especially in dishwashing tablets. Among suitable reactive chlorine-or bromine-oxidizing materials are heterocyclic N-bromo and N-chloro imides such as trichloroisocyanuric, tribromoisocyanuric, dibromoisocyanuric and dichloroisocyanuric acids, and salts thereof with water-solubilising cations such as potassium and sodium. Hydantoin compounds such as 1,3-dichloro-5,5-dimethylhydantoin are also quite suitable.

[0085] Particulate, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium, sodium or calcium hypochlorite and hypobromite. Chlorinated trisodium phosphate and chloroisocyanurates are also suitable bleaching materials.

Water-Soluble Disintegration-Promoting Particles

[0086] A tablet or a region of a tablet may contain water-soluble particles which act to promote disintegration.

[0087] Such soluble particles typically contain at least 40% (of their own weight) of one or more materials selected from

- compounds with a water-solubility exceeding 50 grams per 100 grams water
- phase I sodium tripolyphosphate
- sodium tripolyphosphate which is partially hydrated so as to contain water of hydration in an amount which is at least 0.5% by weight of the sodium tripolyphosphate in the particles.

[0088] As will be explained further below, these disintegration-promoting particles can also contain other forms of tripolyphosphate or other salts within the balance of their composition.

[0089] If the material in such water-soluble disintegration-promoting particles can function as a detergency builder, (as is the case with sodium tripolyphosphate) then of course it contributes to the total quantity of detergency builder in the tablet composition.

[0090] The quantity of water-soluble disintegration-promoting particles may be from 3 or 5% up to 30 or 40% or more by weight of the tablet or region thereof. The quantity may possibly be from 8% up to 25 or 30% or more. However, a possibility within this invention is that the amount of such water-soluble disintegration-promoting particles is low, below 5% of the tablet or region, reliance being placed on insoluble swellable particles.

[0091] One possibility is that these particles contain at least 40% of their own weight, better at least 50%, of a material which has a solubility in deionised water at 20°C of at least 50 grams per 100 grams of water.

[0092] These particles may provide material of such solubility in an amount which is at least 7 wt% or 12 wt% of the composition of the tablet or discrete region thereof.

[0093] A solubility of at least 50 grams per 100 grams of water at 20°C is an exceptionally high solubility: many materials which are classified as water soluble are less soluble than this.

[0094] Some highly water-soluble materials which may be used are listed below, with their solubilities expressed as grams of solid to form a saturated solution in 100 grams of water at 20°C:-

Material	Water Solubility (g/100g)
Sodium citrate dihydrate	72
Potassium carbonate	112
Urea	>100
Sodium acetate	119
Sodium acetate trihydrate	76
Magnesium sulphate 7H ₂ O	71

[0095] By contrast the solubilities of some other common materials at 20°C are:-

Material	Water Solubility (g/100g)
Sodium chloride	36
Sodium sulphate decahydrate	21.5
Sodium carbonate anhydrous	8.0
Sodium percarbonate anhydrous	12
Sodium perborate anhydrous	3.7
Sodium tripolyphosphate anhydrous	15

[0096] Preferably this highly water soluble material is incorporated as particles of the material in a substantially pure form (i.e. each such particle contains over 95% by weight of the material). However, the said particles may contain material of such solubility in a mixture with other material, provided that material of the specified solubility provides at least 40% by weight of these particles.

[0097] A preferred material is sodium acetate in a partially or fully hydrated form.

[0098] A highly water-soluble salt which dissolves in water in an ionised form can be beneficial because as such a salt dissolves it leads to a transient local increase in ionic strength which can assist disintegration of the tablet by preventing nonionic surfactant from swelling and inhibiting dissolution of other materials. This has principal applicability in the context of tablets with a substantial content of surfactant, notably for fabric washing.

[0099] Another possibility is that the said particles which promote disintegration are particles containing sodium tripolyphosphate with more than 40% (by weight of the particles) of the anhydrous phase I form. Such sodium tripolyphosphate has been discussed above as a detergency builder. It may be used in substantial percentages such as 50% or more, of a region in accordance with this invention containing plastically deformable material.

Other Ingredients

[0100] Tablets may also contain 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 for fabrics 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 Genencor, and Alcalase (Trade Mark), and Savinase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

[0101] Enzymes for ware washing are lipases, amylases and proteases. The enzymes most commonly used in machine dishwashing compositions are amylolytic enzymes. Preferably the composition also contains a proteolytic enzyme.

[0102] 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 5.0% by weight of the composition; and these granules or marumes present no problems with respect to compaction to form a tablet.

Chelating Agent

[0103] A chelating agent for metal ions (often referred to as a metal ion sequestrant) may be present in the composition. If present it is preferable that the level of chelating agent is from 0.5 to 3 wt% of the total composition. It can function to stabilise bleach against premature decomposition catalysed by transition metals and/or to inhibit calcium carbonate scale formation.

[0104] Preferred chelating agents include organic phosphonates, amino carboxylates, polyfunctionally-substituted compounds, and mixtures thereof.

[0105] Particularly preferred chelating agents are organic phosphonates such as α -hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethylene 1,1 diphosphonate. Most preferred is hydroxy-ethylene 1,1 diphosphonate, 2 phosphono-1,2,4 butanetricarboxylic acid or salts thereof.

Anti-tarnishing Agents

[0106] Anti-tarnishing agents such as benzotriazole and those described in EP 723577 (Unilever) may be included in tablets for warewashing and dishwashing.

Other Optional Ingredients

[0107] Tablets for fabric washing may also contain a fluorescer (optical brightener), for example Tinopal TM, 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.

[0108] An antifoam material is advantageously included in tablets for fabric washing where substantial amounts of organic surfactant is present, 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, sorbed 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.

[0109] Further ingredients which can optionally be employed include perfumes, colourants or coloured speckles. Fabric washing tablets may include fabric softeners and/or anti-redeposition agents such as linear sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl cellulose.

[0110] Machine dishwashing tablets may include polymers to inhibit scale formation and polymers to inhibit spotting on glassware.

Preparation of Particulate Compositions

[0111] A composition for compaction into a region of a tablet according to this invention, including a plastically deformable and water-soluble material to give a glossy surface, may be made by simply mixing its ingredient materials in particulate form. Granulation of the materials is possible but we have not found it helpful.

[0112] Compositions for other, matte-surfaced regions of a ware washing tablet containing at most a small percentage of surfactant can be prepared by spray-drying, by granulation or by mixing the ingredient materials in particulate form. The nonionic surfactant may be heated and sprayed onto some or all of the particulate solids.

[0113] Compositions for matte-surfaced regions of bleach-containing tablets may also contain a small percentage of surfactant or none at all, and can be prepared in a similar manner.

[0114] In fabric-washing tablets the matte-surfaced regions are likely to contain substantial proportions of surfactant. These compositions can be made by simple mixing of ingredients. However, it is preferred to make particles which contain the surfactant and other materials, either by spray-drying or by granulation. These may then be mixed with other solids. Particles prepared by spray-drying or granulation may be "base-powder" particles containing organic surfactant and detergency builder, often together with some other ingredients.

[0115] Granular detergent compositions of high bulk density may be prepared by granulation and densification in a high-speed mixer/granulator, as described and claimed in EP 340013A (Unilever), EP 352135A (Unilever), and EP 424277A (Unilever) or by the continuous granulation/densification processes described and claimed in EP 367339A

(Unilever) and EP 390251A (Unilever).

[0116] Preferably the particulate composition used to form a matte-surfaced region of a tablet has an average particle size in the range from 200 to 2000 μ m may be eliminated by sieving before tableting, if desired, although we have observed that this is not always essential. Notably fine particles of sodium tripolyphosphate rich in the phase I form, as described above, may be included.

Product Forms and Proportions

[0117] As indicated already, a tablet for fabric washing will generally contain, overall, from 5 to 50% by weight of surfactant and from 5 to 80% by weight of detergency builder which is a water-softening agent. Water-soluble disintegration promoting particles may be present in an amount from 5% to 25% by weight of the composition. Peroxygen bleach may be present and if so is likely to be in an amount not exceeding 25% by weight of the total composition.

[0118] The invention may be embodied as tablets whose principal or sole function is that of removing water hardness. In such tablets the water-softening agent, i.e. detergency builder, especially water-insoluble aluminosilicate, may provide from 50 to 98% of the tablet composition.

[0119] Water-softening tablets may include small percentage of surfactant.

[0120] The invention may be embodied as tablets for machine dishwashing. Such tablets typically contain a high proportion of water soluble salts, such as 50 to 95% by weight, at least some of which, exemplified by sodium tripolyphosphate, sodium citrate and sodium silicate, have water-softening properties.

[0121] Tablets for use as a bleaching additive will typically contain a high proportion of peroxygen bleach, such as 25 to 85% by weight of the composition. This may be mixed with other soluble salt as a diluent. The composition of such a tablet may well include a bleach activator such as tetraacetyethylene diamine (TAED). A likely amount would lie in the range from 1 to 20% by weight of the composition.

[0122] The invention may be embodied in tablets for machine cleaning. Such tablets typically contain a high proportion of citric acid (either anhydrous or hydrated) mixed with small amounts of nonionic surfactant, colouring and perfume.

Tableting

[0123] Tableting entails compaction of a particulate composition. A variety of tableting machinery is known, and can be used. Generally it will function by stamping a quantity of the particulate composition which is confined in a mould.

[0124] The mould in which the tablet is formed may be provided by an aperture within a rigid structure and a pair of punches which can be urged into the aperture towards each other, thereby compacting the contents of the aperture. A tableting machine may have a rotary table defining a number of apertures each with a pair or associated punches which can be driven into an apertures. Each punch may be provided with an elastomeric layer on its surface which contacts the tablet material, as taught in WO 98/46719 or WO 98/46720.

[0125] To make a tablet with multiple layers, the composition of one layer is first put in the mould and compacted. The upper punch is then removed and the composition for the next layer is added on top of the layer already formed. The punches are then urged together again to compact this next layer. If there is to be a third layer the upper punch is removed again and the composition for the third layer is put into the mould.

[0126] After the composition for the last layer is put into the mould a greater compaction force is finally applied. This completes the compaction of all the layers.

[0127] The final compaction pressure used to make machine dishwashing tablets, bleach tablets or other tablets containing not more than 78% by weight surfactant is likely to lie in a range from 50 to 250 Mpa (e.g. 50 to 200kN applied to a tablet cross section of 9 to 10cm²).

[0128] The final compaction pressure used to make fabric washing tablets with a surfactant content over 7% is likely to be in a range from 4 to 40 Mpa (e.g. 6 to 60 kN applied to a tablet cross section of about 15cm²).

[0129] 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. If any heat is supplied, it is envisaged that this will be supplied conventionally, such as by passing the particulate composition through an oven, rather than by any application of microwave energy.

[0130] 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 for fabric washing preferably lies in a range from 1040 or 1050gm/litre preferably at least 1100gm/litre up to 1400gm/litre. The tablet density may well lie in a range up to no more than 1350 or even 1250gm/litre. The overall density of a

tablet of some other cleaning composition, such as a tablet for machine dishwashing or as a bleaching additive, may range up to 1700gm/litre and will often lie in a range from 1300 to 1550gm/litre.

Tablet Strength

[0131] If tablets are cylindrical, a test of tablet strength can be carried out by placing a cylindrical tablet between flat-surfaced platens of a materials testing machine, so that the platens contact a curved surface of the cylinder at either end of a diameter through the tablet. The sample tablet is then compressed diametrically, suitably by advancing the platens of the machine towards each other at a slow rate such as 1cm/min until fracture of the tablet occurs at which point the applied load required to cause fracture is recorded. A value termed the diametral fracture stress can then be calculated from the following equation:

$$\delta_o = \frac{2F_{\max}}{\pi Dt}$$

where δ_o is the diametral fracture stress (in Pascal), $F_{\max}$ is the applied load (in Newtons) at fracture, D is the tablet diameter (in metres) and t is the tablet thickness (in metres).

[0132] If a tablet has a rectangular cross section a similar test of strength is carried out by placing the tablet on its longer edge on one platen of a materials testing machine and using the other platen to drive a wedge against the opposite surface. This form of test can also be applied to cylindrical tablets. It has been found that both tests give similar values for the expression

$$\frac{F_{\max}}{(s.t)}$$

where s is the distance between the points of contact with the tablet, i.e. the distance from wedge tip to opposite platen, or the diameter of a cylindrical tablet and t is the tablet thickness.

[0133] Suitable values of force at fracture for a rectangular machine dishwashing tablet with a width of 25mm and thickness of 15 to 20 mm are 70 to 200kN.

[0134] Suitable values of force at fracture for a fabric washing tablet with a diameter of 40 to 45 mm and a thickness of 15 to 25mm are 12 to 75 kN, approximately corresponding to a DFS of 10 to 60 kPa, more preferably at least 25 kN, approximately corresponding to a DFS of at least 20 kPa.

Example 1

[0135] A three layer tablet for machine dishwashing.

[0136] A particulate composition for matte-surfaced regions was prepared by mixing the following ingredients.

Material	% by weight
Sodium tripolyphosphate (partially hydrated)	48%
Sodium disilicate granules	9%
Sodium sulphate	8%
Nonionic detergent	5.5%
Sodium perborate monohydrate	16.5%
TAED	2.8%
Manganese catalyst	1.1%
Sodium polyacrylate	3.7%
Enzyme granules (also containing sodium carbonate)	4.5%

(continued)

Material	% by weight
Benzotriazole, heavy metal sequestrant and perfume	0.9%
TOTAL	100%

[0137] A second particulate composition for making glossy-surfaced regions was made by mixing

Material	% by weight
Sodium tripolyphosphate (Rhodiaphos HPA 3.5)	50%
Polyethylene glycol (PEG 4000)	47.5%
Heavy metal sequestrant	2.5%
Food grade green dye	0.01%

[0138] Three layer tablets were made by

- i) introducing 9gm of the first composition into a mould of a tableting press, compacting the composition and opening the mould,
- ii) putting 4gm of the second composition into the mould on top of the compacted first composition, compacting the contents of the mould and then opening the mould again,
- iii) putting a further 9gm of the first composition into the mould, on top of the compacted second composition, then compacting the entire contents of the mould with more force than in the previous two steps, next opening the mould and ejecting the tablet from the mould.

[0139] The tablet had a rectangular cross section of 36mm by 26mm and a thickness of 15 to 20 mm. It had identical top and bottom layers of the first composition. These are white, with a matte surface. Sandwiched between them was a thin middle layer of the second composition. It was visible at the edge of the tablet and its exposed surface had a glossy appearance. It appeared somewhat translucent as well as green in colour.

[0140] This example was also carried out using an unstable green dye. After several weeks storage, the dye had faded so that it had almost completely lost its colour. However, the middle layer still had a smooth glossy appearance at its exposed surface and thus remained visually distinct.

Example 2

[0141] A three layer tablet for machine dishwashing. Two particulate compositions are prepared by mixing the ingredients in the following table.

	% by weight	
	A	B
Sodium tripolyphosphate (partially hydrated)	44%	52%
Sodium disilicate granules	9%	9%
Sodium sulphate	4%	12%
Nonionic detergent	5.4%	5.6%
Sodium perborate monohydrate	33%	0%
TAED	0%	5.6%
Manganese catalyst	0%	2.2%
Sodium polyacrylate	3.7%	3.7%

(continued)

	% by weight	
	A	B
Enzyme granules (also containing sodium carbonate)	0%	9%
Benzotriazole, heavy metal sequestrant and perfume	0.9%	0.9%
total	100%	100%

[0142] Three layer tablets are made generally as in Example 1. The first layer was made from 9gm of composition A containing perborate. The middle layer is the same as in Example 1. The third layer is made from 9gm of composition B containing bleach activators and enzymes. Consequently there is no contact between the perborate and the bleach activators and enzymes until the tablets dissolve in water at the time of use.

Example 3

[0143] Three layer tablets for fabric washing. Detergent base powder, incorporating organic surfactants and detergent builder was made using the process described in WO-A-98/11193. The powder had the following compositions. Amounts are shown both as weight percentages of the base powder and as parts by weight.

Ingredient		
	(wt%)	Parts by Weight
Sodium linear alkylbenzene sulphonate	23.60	10.15
Nonionic surfactant (C13-15 branched fatty alcohol 7EO)	7.05	3.03
Soap	1.65	0.71
Zeolite A24 (Zeolite MAP from Crosfields)	40.61	17.46
Sodium acetate trihydrate	10.21	4.39
Sodium carbonate	4.97	2.14
Linear sodium carboxymethyl cellulose (SCMC)	0.92	0.40
Sodium citrate dihydrate	3.06	1.32
Linear sodium sulphate, moisture and minor ingredients	7.93	3.41
Total	100	43.00

[0144] The amount of zeolite MAP (zeolite A24) in the table above is the amount which would be present if it was anhydrous. Its accompanying small content of moisture is included as part of the moisture and minor ingredients. Linear sodium carboxymethyl cellulose is a commonly used water soluble antiredeposition polymer.

[0145] Disintegrant particles were made from about 95% microcrystalline cellulose as carrier and 5% cross-linked carboxymethyl cellulose as swellable disintegrant with a balance of soluble salt. When microcrystalline cellulose comes into contact with water, it expands to about 1.5 times its dry volume. Cross-linked carboxymethyl cellulose expands considerably when brought into contact with water, swelling to approximately 3 times its original dry volume. This combination of materials was supplied by FMC Corporation under designation Nylin LX-16.

[0146] A particulate composition was made using base powder as above, disintegrant particles as above, PEG 1500 in the form of powder of average particle size 150 micrometers and various particulate ingredients as follows:

Ingredients	% by weight
Base Powder	43
Sodium percarbonate coated with sodium chloride	15.0
TAED granules	5.0

(continued)

Ingredients	% by weight
Anti-foam granules	1.7
Soil-release polymer	1.0
Fluorescer granules	1.2
Sodium silicate granules	3.0
Acrylate/maleate copolymer	1.0
Sodium acetate trihydrate	20
Blue speckles and heavy metal sequestrants	2.0
Nylin LX-16	3.5
PEG 1500	3.6
Total	100

[0147] A second particulate composition consists of:

Ingredients	% by weight
PEG 4000	50%
Sodium citrate dihydrate	40%
Enzyme granules	10%

[0148] The tablets are made as three layer tablets, with a 4gm layer of the second composition sandwiched between two 19gm layers of the first composition.

Claims

1. A three-layer tablet of cleaning composition in which a discrete region of the tablet providing at least part of the tablet exterior is a compacted particulate composition containing at least 10% by weight of the composition of the region, of water-soluble material, plastically deformable under pressure and melting at a temperature in a range from 30° to 90°C, wherein solid particulate material which is mixed with the plastically deformable material has an average particle size of 500 micrometers or less and wherein the discrete region is the middle layer of the three layers.
2. A tablet according to claim 1, wherein the said water-soluble, plastically deformable material melts at a temperature in a range from 40° to 80°C.
3. A tablet according to any one of the preceding claims wherein the said water-soluble, plastically deformable material is nonionic.
4. A tablet according to any one of the preceding claims wherein the said water-soluble, plastically deformable material is an organic polymer.
5. A tablet according to any one of the preceding claims wherein the said water-soluble, plastically deformable material contains polyoxyethylene chains in which the average number of ethylene oxide residues is at least 20.
6. A tablet according to any one of the preceding claims wherein the other particulate solid has a mean particle size not exceeding 400 micrometers.

Patentansprüche

1. Dreischichttablette für eine Reinigungszusammensetzung, worin ein diskreter Bereich der Tablette, der mindestens einen Teil des Tablettenäußeren bereitstellt, eine verdichtete, teilchenförmige Zusammensetzung darstellt, die mindestens 10 Gew.-% der Zusammensetzung des Bereichs von in Wasser löslichem, unter Druck plastisch verformbarem und bei einer Temperatur in einem Bereich von 30° bis 90°C schmelzendem Material enthält, wobei festes, teilchenförmiges Material, das mit dem plastisch verformbaren Material vermischt ist, eine mittlere Teilchengröße von 500 Mikrometern oder weniger aufweist und wobei der diskrete Bereich die mittlere Schicht der drei Schichten darstellt.
2. Tablette nach Anspruch 1, worin das in Wasser lösliche, plastisch verformbare Material bei einer Temperatur in einem Bereich von 40° bis 80°C schmilzt.
3. Tablette nach einem der vorangehenden Ansprüche, worin das in Wasser lösliche, plastisch verformbare Material nichtionisch ist.
4. Tablette nach einem der vorangehenden Ansprüche, worin das in Wasser lösliche, plastisch verformbare Material ein organisches Polymer darstellt.
5. Tablette nach einem der vorangehenden Ansprüche, worin das in Wasser lösliche, plastisch verformbare Material Polyoxyethylenketten enthält, worin die mittlere Zahl von Ethylenoxidresten mindestens 20 ist.
6. Tablette nach einem der vorangehenden Ansprüche, worin der andere teilchenförmige Feststoff eine mittlere Teilchengröße aufweist, die 400 Mikrometer nicht übersteigt.

Revendications

1. Pastille de composition nettoyante à trois couches dans laquelle une région discrète de la pastille qui fournit au moins une partie de l'extérieur de la pastille est une composition particulière compactée contenant, à hauteur d'au moins 10 % en poids de la composition de la région, un matériau hydrosoluble, plastiquement déformable sous pression et ayant une température de fusion se situant dans la gamme allant de 30° à 90°C, dans laquelle ledit matériau particulier qui est mélangé avec le matériau plastiquement déformable a une taille moyenne de particule de 500 micromètres ou inférieure et dans laquelle la région discrète est la couche du milieu parmi les trois couches.
2. Pastille selon la revendication 1, dans laquelle ledit matériau hydrosoluble, plastiquement déformable, fond à une température se situant dans la gamme allant de 40°C à 80°C.
3. Pastille selon l'une quelconque des revendications précédentes, dans laquelle ledit matériau hydrosoluble, plastiquement déformable, est non ionique.
4. Pastille selon l'une quelconque des revendications précédentes, dans laquelle ledit matériau hydrosoluble, plastiquement déformable, est un polymère organique.
5. Pastille selon l'une quelconque des revendications précédentes, dans laquelle ledit matériau hydrosoluble, plastiquement déformable, contient des chaînes de polyoxyéthylène dans lesquelles le nombre moyen de résidus d'oxyde d'éthylène est d'au moins 20.
6. Pastille selon l'une quelconque des revendications précédentes, dans laquelle l'autre solide particulière a une taille moyenne de particule ne dépassant pas 400 micromètres.