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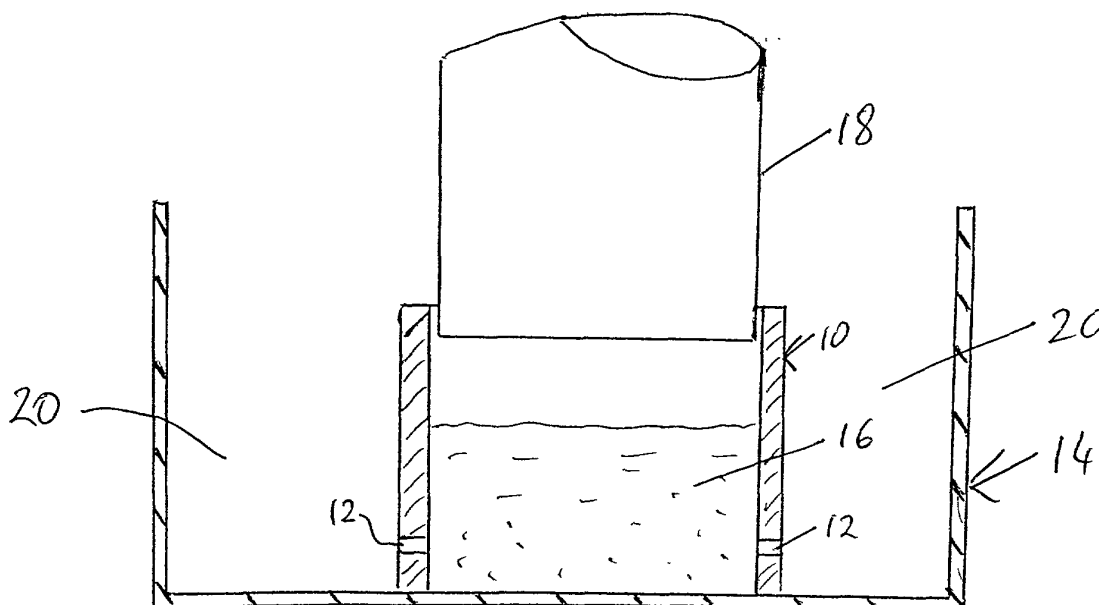
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(54) **Cleaning compositions**

(57) Tablets of a cleaning composition containing at least one of: surfactant, detergency builder, bleach are made from a composition which incorporates 0.5 to 10%

of disintegration-promoting particles which contain crosslinked polyvinyl pyrrolidone. The composition may provide the whole tablet, or a region such as a layer.



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Description

[0001] This invention relates to cleaning compositions in the form of tablets. These tablets are intended to disintegrate when placed in water and thus are intended to be consumed in a single use. The tablets may be suitable for use in machine dishwashing, the washing of fabrics or other cleaning tasks.

[0002] 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) and are now sold commercially. Tablets containing bleach for use as an additive to a fabric washing liquor have been disclosed in US-A-4013581 (Huber/Procter and Gamble). Tablets containing a water softening agent, for use as an additive in cleaning, are sold commercially and are one form of tablet disclosed in EP-A-838519 (Unilever). Tablets of composition suitable for machine dishwashing have been disclosed in EP-A-318204 and are sold commercially. Tablets have several advantages over powdered products: they do not require measuring and are thus easier to handle and dispense into the washload, and they are more compact, hence facilitating more economical storage.

[0003] Tablets of a cleaning composition are generally made by compressing or compacting a composition in particulate form. Although it is desirable that tablets have adequate strength when dry, yet disperse and dissolve quickly when brought into contact with water, it can be difficult to obtain both properties together. Tablets formed using a low compaction pressure tend to crumble and disintegrate on handling and packing; while more forcefully compacted tablets may be sufficiently cohesive but then fail to disintegrate or disperse to an adequate extent in the wash. Tableting will often be carried out with enough pressure to achieve a compromise between these desirable but antagonistic properties. However, it remains desirable to improve one or other of these properties without detriment to the other so as to improve the overall compromise between them.

[0004] If a tablet contains organic surfactant, this functions as a binder, plasticising the tablet. However, it can also retard disintegration of the tablet by forming a viscous gel when the tablet comes into contact with water. Thus, the presence of surfactant can make it more difficult to achieve both good strength and speed of disintegration: the problem has proved especially acute with tablets formed by compressing powders containing surfactant and built with insoluble detergency builder such as sodium aluminosilicate (zeolite) including the forms of zeolite P described and claimed in EP 384070 (Unilever)

[0005] EP-A-466484 is concerned with detergent tablets compacted from a composition of particles which have a restricted particle size distribution such that at least 90% of the composition falls between upper and lower limits on particle size which differ from each other by not more than 700 micrometers. This document and EP 522766 disclose tablets made from surfactant-containing particles bearing a coating of a material which functions as a binder and also serves as a tablet disintegrant. One material which is used as such a coating is cross-linked polyvinyl pyrrolidone. In examples, this is sprayed on as a solution in acetone giving a thin coating on the particles. An approximate calculation indicates a coating thickness substantially below 50 micrometers.

[0006] Subsequent documents have used other routes to enhance tablet disintegration.

[0007] It is known to include materials whose function is to enhance disintegration of tablets when placed in wash water. For example, our EP-A-838519 mentioned above teaches the use of sodium acetate trihydrate for this purpose.

[0008] A number of documents have taught that the disintegration of tablets of cleaning composition can be accelerated by incorporating in the tablet a quantity of a water-insoluble but water-swelling material serving to promote disintegration of the tablet when placed in water at the time of use. Notably, these include WO 98/40462 and WO 98/40463 in which the disintegrant material is a form of cellulose.

[0009] We have now found that particulate cross-linked polyvinyl pyrrolidone is unexpectedly effective as a tablet disintegrant when mixed into a particulate cleaning composition.

[0010] According to a first aspect of this invention, there is provided a tablet of a compacted particulate cleaning composition containing at least one cleaning ingredient which is an organic surfactant, a water softening agent or a bleach, wherein the tablet or a discrete region of the tablet contains 0.5% up to 10%, by weight of the tablet or region of disintegrant particles which contain cross-linked polyvinyl pyrrolidone. These disintegrant particles preferably do not contain surfactant or bleach.

[0011] When the tablet is placed in water the cross-linked polyvinyl pyrrolidone swells, and this causes or assists disintegration of the tablet or region of a tablet.

[0012] This invention is particularly applicable when the tablets contain both surfactant and detergency builder, as in tablets for fabric washing.

[0013] In a preferred form, the present invention provides a detergent tablet of compacted particulate composition containing organic surfactant, detergency builder and optionally other ingredients, wherein the tablet or a discrete region thereof comprises

i) 20 to 99% by weight of particles which contain surfactant mixed with other material

ii) 1 to 10% of disintegrant particles with mean size greater than 200, better 250 micrometers which contain cross-

linked polyvinyl pyrrolidone

iii) 0 to 79% of other particulate ingredients.

[0014] Preferably these disintegrant particles (ii) do not contain surfactant. Possibly they do not contain bleach.

[0015] This invention also provides, in a second aspect, a method of making a tablet comprising mixing up to 10% of disintegrant particles of size greater than 250 micrometers and other particulate material to form a cleaning composition, and compacting that composition to form a tablet or a region of a tablet.

[0016] Forms of this invention, preferred and optional features, and materials which may be used, will now be discussed in greater detail.

Discrete Regions/Whole Tablets

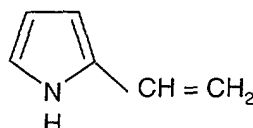
[0017] A tablet of the invention may be either homogeneous or heterogeneous. In the present specification, the term "homogeneous" is used to mean a tablet produced by compaction of a single particulate composition, but does not imply that all the particles of that composition will necessarily be of identical composition. The term "heterogeneous" is used to mean a tablet consisting of a plurality of discrete regions, for example layers, inserts or coatings, each of which is a matrix of particles derived by compaction from a particulate composition. In a heterogeneous tablet according to the present invention, each discrete region of the tablet will preferably have a mass of at least 3gm.

[0018] In a heterogeneous tablet, at least one of the discrete regions contains the said disintegrant particles which incorporate cross-linked polyvinyl pyrrolidone. In this event the benefit of the cross-linked polyvinyl pyrrolidone to promote disintegration will be conferred on the region or regions of the tablet which contain the material. This can, if desired, be utilised to cause the different regions of the tablet to disintegrate at different rates, thereby liberating their constituent materials into a wash liquor at differing rates.

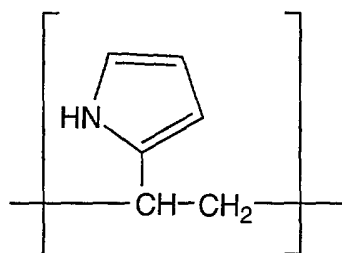
[0019] There are a number of possibilities concerning heterogeneous tablets. Cross-linked polyvinyl pyrrolidone may or may not be included in every region of a heterogeneous tablet, even though the regions differ from each other in some other feature of their composition. Thus disintegrant particles which contain cross-linked polyvinyl pyrrolidone may be present at different concentrations in different tablet regions; they may be present in one region and absent from another; or may be present at equal concentration in every region of the tablet. It is possible that one region will contain disintegrant particles which contain cross-linked polyvinyl pyrrolidone while another region will contain some other water-swellaable material.

Cross-linked Polyvinyl Pyrrolidone

[0020] 2-vinyl pyrrolidone of formula



can be polymerised to a linear polymer containing



repeat units. Such linear polymers are water-soluble. Cross-linked polyvinyl pyrrolidone can be a copolymer of vinyl pyrrolidone and a small amount of a cross-linked co-monomer which is able to become incorporated into more than

one polymer chain and thereby link two polymer chains. The formation of cross links between polymer chains by use of a monomer with multiple reactive groups is well known in polymer chemistry.

[0021] Other routes for cross-linking of polyvinyl pyrrolidone chains have been published.

[0022] Cross-linked polyvinyl pyrrolidone is available commercially from BASF and from ISP corporation.

[0023] It is available as particles with sizes spread over a range. Particles of desired size can be obtained by sieving out particles which are smaller than desired.

[0024] We have recognised, as a key feature of cross-linked polyvinyl pyrrolidone that it swells when it comes into contact with water. If the material is confined - as is the case when it is inside a tablet, the swelling generates a force of expansion which assists tablet disintegration. We have found that a significant property is speed with which this force develops. Cross-linked polyvinyl pyrrolidone has that property to a high degree.

[0025] Disintegrant particles utilised in this invention may consist of cross-linked polyvinyl pyrrolidone alone or as at least 50% by weight of the particles. If a commercial source of cross-linked polyvinyl pyrrolidone is used as supplied, the particles are likely to contain more than 80% by weight of polyvinyl pyrrolidone.

[0026] Another possibility is that the disintegrant particles will contain a minority of cross-linked polyvinyl pyrrolidone mixed with a greater quantity of other material acting as a carrier.

[0027] It is envisaged that such a carrier material will be water-insoluble. Preferably it swells to some extent on contact with water, although not as much as the cross-linked polyvinyl pyrrolidone.

[0028] Possible carrier materials are starches, for example, maize, rice and potato starches, celluloses, for example Arbocel®-B and Arbocel®-BC (beech cellulose), Arbocel®-BE (beech-sulphite cellulose), Arbocel®-B-SCH (cotton cellulose) and Arbocel®-FIC (pine cellulose) from J Rettenmaier and Söhne in Germany and also microcrystalline cellulosic fibres.

[0029] Whether the disintegrant particles have a majority or minority of cross-linked polyvinyl pyrrolidone it is desirable that the particles have a mean particle size of at least 200, better at least 250 and preferably at least 350 micrometers.

[0030] The disintegrant particles may have a size distribution such that at least 75% by weight of the particles have a particle size of 200 micrometers or above, and the mean particle size is at least 250 micrometers.

[0031] Such a size and size distribution may be obtained as a result of the process by which the particles are made, or it may be achieved by sieving to remove undersized particles.

[0032] The amount of disintegrant particles containing cross-linked polyvinyl pyrrolidone is preferably from 1 to 8% of the composition, better from 1 to 5%.

Surfactant Compounds

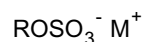
[0033] Compositions which are compacted to form tablets or tablet regions of this invention may contain one or more organic detergent surfactants. In a fabric washing composition, these preferably provide from 5 to 50% by weight of the overall tablet composition, more preferably from 8 or 9% by weight 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.

[0034] 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.

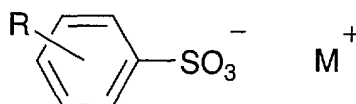
[0035] In a machine dishwashing composition, organic surfactant is likely to constitute from 0.5 to 8%, more likely from 0.5 to 4.5% of the overall composition and is likely to consist of nonionic surfactant, either alone or in a mixture with anionic surfactant.

[0036] 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 C₈-C₁₅; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0037] 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.



[0038] 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.

[0039] 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.

[0040] 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.

[0041] 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.

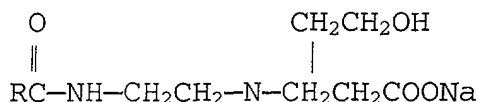
[0042] Suitable nonionic surfactant compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide.

[0043] 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.

[0044] 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.

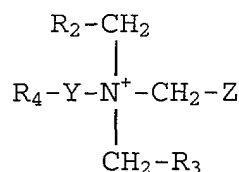
[0045] In certain forms of this invention the amount of nonionic surfactant lies in a range from 4 to 40%, better 4 or 5 to 30% by weight of the composition. Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition, prior to compaction into tablets.

[0046] Amphoteric surfactants which may be used jointly with anionic or nonionic surfactants or both include amphopropionates of the formula:



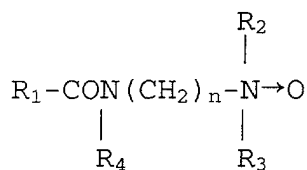
where RCO is a acyl group of 8 to 18 carbon atoms, especially coconut acyl.

[0047] 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).

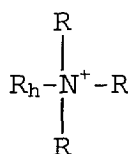
[0048] Another example of amphoteric surfactant is amine oxide of the formula



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.

[0049] 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.

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.

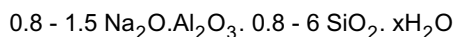
Water-softening agent

[0050] A composition which is compacted to form tablets or tablet regions may contain a so-called water-softening agent which serves to remove or sequester calcium and/or magnesium ions in the water. In the context of a detergent composition containing organic surfactant, a water-softening agent is more usually referred to as a detergency builder.

[0051] When a water-softening agent is present, the amount of it is likely to lie in a broad range from 5 better 15 wt% up to 98% of the tablet composition. In detergent tablets the amount is likely to be from 15 to 80%, more usually 15 to 60% by weight of the tablet.

[0052] Water-softening agents 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.

[0053] Alkali metal aluminosilicates are strongly favoured as environmentally acceptable water-insoluble softening agents (detergency builders) for fabric washing. Alkali metal (preferably sodium) aluminosilicates may be either crystalline or amorphous or mixtures thereof, having the general formula:



[0054] 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.

[0055] Suitable crystalline sodium aluminosilicate ion-exchange 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".

[0056] Conceivably a water-insoluble water-softener (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 $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ 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.

[0057] The category of water-soluble phosphorus-containing inorganic softeners includes the alkali-metal orthophosphates, metaphosphates, pyrophosphates and polyphosphates. Specific examples of inorganic phosphate detergency builders include sodium and potassium tripolyphosphates, orthophosphates and hexametaphosphates.

[0058] Non-phosphorus water-soluble water-softening agents 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 and hydroxyethyliminodiacetates.

[0059] 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 the wash liquor.

Bleach System

[0060] 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.

[0061] 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.

Water-Soluble Disintegration-Promoting Particles

[0062] A tablet or a region of a tablet may contain water-soluble particles to promote disintegration, in addition to the water-swellable, water-insoluble particles containing cross-linked polyvinyl pyrrolidone as required by this invention.

[0063] Such soluble particles typically contain at least 40% (of their own weight) of one or more salts 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.

[0064] 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.

[0065] 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.

[0066] The quantity of water-soluble disintegration-promoting particles may be from 3 or 5% up to 30 or 40% by weight of the tablet or region thereof. The quantity may possibly be from 8% up to 25% or 30% or more (especially if this salt also functions as a detergency builder). However, it is within this invention that the amount of such water-soluble disintegration-promoting particles is low, between 2% and 8% of the tablet or region, reliance being placed on particles containing cross-linked polyvinyl pyrrolidone.

[0067] One possibility is that these water-soluble disintegration-promoting particles contain at least 40% of their own weight, better at least 50%, of a salt which has a solubility in deionised water at 20°C of at least 50 grams per 100 grams of water.

[0068] These particles may provide salt 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.

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[0069] A solubility of at least 50 grams per 100 grams of water at 20°C is an exceptionally high solubility: many salts are classified as water soluble are less soluble than this.

[0070] Some highly water-soluble salts 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	Solubility (g/100g)
Sodium citrate dihydrate	72
Potassium carbonate	112
Sodium acetate	119
Sodium acetate trihydrate	76
Magnesium sulphate 7H ₂ O	71

[0071] 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

[0072] Preferably this highly water soluble salt is incorporated as particles of the salt in a substantially pure form (i. e. each such particle contains over 95% by weight of the salt). However, the said particles may contain salt of such solubility in a mixture with other material, provided that salt of the specified solubility provides at least 40% by weight of these particles.

[0073] A preferred salt is sodium acetate in a partially or fully hydrated form.

[0074] As a highly water-soluble 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.

[0075] Another possibility is that water-soluble particles which promote disintegration are particles containing sodium tripolyphosphate with more than 40% (by weight of the particles) of the anhydrous phase I form.

[0076] Sodium tripolyphosphate is very well known as a sequestering builder in detergent compositions. It exists in a hydrated form and two crystalline anhydrous forms. These are the normal crystalline anhydrous form, known as phase II which is the low temperature form, and phase I which is stable at high temperature. The conversion of phase II to phase I proceeds fairly rapidly on heating above the transition temperature, which is about 420°C, but the reverse action is slow. Consequently phase I sodium tripolyphosphate is metastable at ambient temperature.

[0077] 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.

[0078] Particles which contain this phase I form will often contain the phase I form of sodium tripolyphosphate as at least 50% or 55% by weight of the tripolyphosphate in the particles.

[0079] Suitable material is commercially available. Suppliers include Rhone-Poulenc, France and Albright & Wilson, UK.

[0080] Another possibility is that this sodium tripolyphosphate is partially hydrated. The extent of hydration should be at least 0.5% by weight of the sodium tripolyphosphate in the particles. It may lie in a range from 0.5 to 4%, or it may be higher, e.g. up to 9 or 10% by weight of the sodium tripolyphosphate.

[0081] It is possible that water-soluble particles which promote disintegration contain at least 40 wt% sodium tripolyphosphate which has a phase I content of at least 50% by weight of the tripolyphosphate but is also sufficiently hydrated so as to contain at least 0.5% water by weight of the sodium tripolyphosphate.

[0082] The remainder of the tablet composition used to form the tablet or region thereof may include additional sodium tripolyphosphate. This may be in any form, including sodium tripolyphosphate with a high content of the anhydrous phase II form.

[0083] This invention is particularly envisaged for use in tablets where the composition of the tablet or region of the tablet which incorporates cross-linked polyvinyl pyrrolidone contains not more than 15% possibly not more than 12% or 10% by weight of water-soluble constituents with an above mentioned water-solubility of at least 50 grams per 100 grams of water at 20°C.

Other Ingredients

[0084] Tablets of the invention 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 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.

[0085] The tablets of the invention may also contain 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.

[0086] An antifoam material is advantageously included if 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.

[0087] It may also be desirable that a 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. A composition for fabric washing will generally not contain more than 15 wt% silicate. A tablet for machine dishwashing will frequently contain at least 20 wt% silicate.

[0088] Further ingredients which can optionally be employed in fabric washing detergent tablets of the invention include anti-redeposition agents such as sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone which inhibits dye transfer, 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.

Particle Size and Distribution

[0089] A tablet of this invention, or a discrete region of such a tablet, is a matrix of compacted particles.

[0090] Preferably the particulate composition has an average particle size in the range from 200 to 2000 μm , more preferably from 250 to 1400 μm . Fine particles, smaller than 180 μm or 200 μm may be eliminated by sieving before tableting, if desired, although we have observed that this is not always essential.

[0091] This invention may be employed when the tablet or region of a tablet has a wider particle size distribution than the narrow range recommended by EP-A-466484. Thus, if the particle size distribution of the composition which is compacted is such that 5% by weight of the composition consists of particles smaller than a size which may be referred to as the "lower boundary" and 5% by weight of the composition consists of particles larger than a value referred to as the "upper boundary" the upper boundary may well be more than 700 micrometers greater than the lower boundary.

[0092] Size of the disintegrant particles has been discussed above.

[0093] While the starting particulate composition may in principle have any bulk density, the present invention may be especially relevant to tablets of detergent composition 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.

[0094] Thus the starting particulate composition may suitably have a bulk density of at least 400 g/litre, preferably at least 500 g/litre, and possibly at least 600 g/litre.

[0095] A composition which is compacted into a tablet or tablet region may contain particles which have been prepared by spray-drying or granulation and which contain a mixture of ingredients. Such particles may contain organic detergent surfactant and some or all of the water-softening agent (detergency builder) which is also present in a detergent tablet.

[0096] Granular detergent compositions of high bulk density prepared by granulation and densification in a high-speed mixer/granulator, as described and claimed in EP 340013A (Unilever), EP 352135A (Unilever), and EP 425277A (Unilever), or by the continuous granulation/densification processes described and claimed in EP 367339A (Unilever)

and EP 390251A (Unilever), are inherently suitable for use in the present invention.

[0097] In a process embodying a second aspect of this invention, disintegrant particles containing cross-linked polyvinyl pyrrolidone as required by this invention are mixed with the remainder of the particulate composition prior to compaction. This remainder of the particulate composition preferably includes particles which have been prepared by spray-drying or granulation and which contain organic detergent surfactant mixed with detergency builder and possibly other ingredients. At this stage when the disintegrant particles are mixed with the remainder of the particulate composition, other particulate constituents, notably including any optional water-soluble particles to promote disintegration, may also be mixed into the particulate composition.

Compositions for Tableting

[0098] Compositions intended for compaction to tablets for machine dishwashing, or bleaching or water-softening may be prepared by mixing all of the particulate ingredients together including the electrolyte-impregnated swellable material required by this invention. Detergent compositions for fabric washing may also be made in this way. However it is likely that such compositions will begin with an initial step of preparing a base powder containing surfactant especially ionic surfactant and at least some detergency builder. Preparation of such a base powder may be carried out by spray-drying or by a granulation process. The base powder is then desirably mixed with other ingredients including water-soluble salts to promote disintegration, other constituents of the overall composition such as bleach and bleach activator and the disintegrant particles containing cross-linked polyvinyl pyrrolidone.

[0099] Liquid constituents of the overall composition such as perfume or nonionic detergent may be sprayed on to the resulting mixture before it is compacted into tablets.

Product forms and proportions

[0100] The present invention may especially be embodied as a tablet for fabric washing. Such a tablet 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. Peroxygen bleach may be present and if so is likely to be in an amount not exceeding 25% by weight of the total composition.

[0101] In the case of a heterogeneous tablet, a region which contains water-swellable material in accordance with this invention may also contain surfactant in an amount which is from 5 to 50% by weight of that region and detergency builder in an amount which is from 5 to 80% by weight of that region.

[0102] The invention may be embodied as tablets whose principal or sole function is that of removing water hardness. In such tablets the water-softening agents, especially water-insoluble aluminosilicate, may provide from 50 to 98% of the tablet composition. A water-soluble supplementary builder may well be included, for instance in an amount from 2% to 30wt% of the composition, or may be considered unnecessary and not used.

[0103] Water-softening tablets embodying this invention may include some surfactant.

[0104] 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.

[0105] Both water-softening and machine dishwashing tablets may include nonionic surfactant which can act as a lubricant during tablet manufacture and as a low foaming detergent during use. The amount may be small, e.g. from 0.2 or 0.5% by weight of the composition up to 3% or 5% by weight.

[0106] 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 tetraacetylene diamine (TAED). A likely amount would lie in the range from 1 to 20% by weight of the composition.

Tableting

[0107] 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 die.

[0108] 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.

[0109] The size of a tablet will suitably range from 10 to 160 grams, preferably from 15 to 60 g, depending on the

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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.

The Drawing

[0110] The accompanying drawing is a cross-sectional view which illustrates a piece of apparatus used in conjunction with a materials testing machine.

Example 1

[0111] Measurements were made using the piece of apparatus shown in the attached drawing and an Instron materials testing machine.

[0112] The apparatus consists of a cylinder (10) with internal diameter 25mm and a length of 20mm. This cylinder is perforated by a ring of holes (12) adjacent one end. There are 36 of these holes, of 1mm diameter, with centres 2.5mm from the end of the cylinder.

[0113] This end of the cylinder is glued to the base of a glass container (14) of internal diameter 73mm.

[0114] To test a sample of powdered disintegrant, 1.5 gram of the disintegrant is placed in the cylinder and gently tapped so that it forms a level bed (16) which is usually 6mm to 10mm deep depending on the bulk density of the powder.

[0115] A plunger (18) of the Instron machine is moved into the upper set of the cylinder, over this powder bed.

[0116] Under computer control of the Instron machine the plunger is applied to the top of the powder bed (16) with a force of 1 Newton.

[0117] 50ml of distilled water at 22°C is tipped into the annular space (20) around the cylinder. This water passes through the holes (12) into the powder bed. The Instron machine is programmed to hold the plunger in position against the swelling bed of powder, and the force required for this is recorded. A graph of this force against time is plotted. The slope of the graph is the disintegrating force development rate, and its maximum value is noted.

[0118] It is preferred that a strongly swelling material, if tested, by itself, has ability to absorb at least twice its own volume of water and has a development of expansion force which exceeds 1.5 Newton/second.

[0119] The development of swelling force was measured for a number of materials, as set out in the following table.

Trade Name	Chemical Nature and Supplier	Disintegrating force, max development rate (N/sec)
	Maize starch	1.1
Explotab	Na-carboxy methyl starch ex. Mendell Co	2.0
Primojel	Na-carboxy methyl starch ex Avebe	2.2
Avicel PH 101	Micro crystalline cellulose ex. FMC	0.6
L-HPC	Low substituted hydroxy propyl cellulose ex. Shin-Etsu Japan	2.2
Ac-di-Sol	Cross-linked SCMC ex FMC	3.5
Polyplasdone XL	Cross-linked PVP ex. ISP	4.3
Kollidon CL	Cross-linked PVP ex BASF	4.8
Plas-Vita	Co-polymer of formalin and casein ex. Eigenmann-Veronelli	3.1

[0120] The significant parameter in the third column of the above table is the maximum slope of a graph of expansion force against time.

[0121] Measurement of water-absorption can be recorded with the same apparatus. The plunger is again applied to the top of a bed of the dry powder, and pressed against it with a force of 1 Newton. 50ml of water is poured in as before. The Instron machine is programmed to allow expansion of the bed of powder, while maintaining a force on it of 1

Newton. Displacement of the plunger is recorded.

Example 2

[0122] A detergent base powder was made by a neutralisation and granulation process as described in WO-A-98/11193. The composition of the base powder is shown below:

Ingredient	Parts by Weight
Sodium linear alkylbenzene sulphonate	10.40
Nonionic surfactant (C ₁₃₋₁₅ branched fatty alcohol 7EO)	3.12
Soap	0.55
Zeolite A24 (Zeolite MAP available from Crosfields)	20.20
Sodium acetate trihydrate	2.70
Sodium carbonate (light soda ash)	2.90
Linear sodium carboxymethyl cellulose (SCMC)	0.42
Moisture and impurities	3.70
TOTAL	44.00

[0123] This base powder was sieved to obtain particles between 500 and 1000µm.

[0124] A number of further ingredients were added to this base powder by dry-mixing (except the perfume, which was sprayed on) resulting in the following composition:

Ingredients	Wt%			
	A	B	C	D
Base powder	44.00	44.00	57.20	58.50
Anti-foaming granules	2.00	2.00	2.60	2.66
Fluorescer on sodium carbonate	2.00	2.00	2.60	2.66
Sodium disilicate granules	3.31	3.31	4.32	4.40
Soil release polymer	1.00	1.00	1.30	1.32
TAED granules (83% active)	4.00	4.00	5.22	5.32
Sodium percarbonate (coated)	15.00	15.00	19.53	19.92
Organic phosphonate sequestrants	1.24	1.24	1.61	1.63
Sodium acetate trihydrate	22.00	24.00	0	0
Cross-linked PVP ex BASF, mean particle size 253 micrometers	5.00	3.00	5.00	3.00
Perfume	0.45	0.45	0.60	0.60
TOTAL	100	100	100	100

[0125] It should be noted that the sodium acetate trihydrate and the cross-linked polyvinyl pyrrolidone are both disintegration-promoting particles. The former is highly water-soluble. The latter swells on contact with water.

[0126] The compositions were compacted on a single punch tableting machine, to produce cylindrical tablets with diameter 44mm, weight approximately 40 gm and substantially equal tablet strength.

[0127] The speed of disintegration of the tablets was tested by means of a procedure in which a tablet was placed on a metal grid with holes of 1cm by 1cm and immersed in 1 litre of water at either 10°C or 20°C. If any residue remained after a standard time of 60 seconds, this was recovered and dried enabling the percentage disintegration in 60 seconds to be calculated.

[0128] As comparative example A' another, less effective polymer was used in composition A, in place of polyvinyl pyrrolidone. As comparative examples C' and D' a cellulosic disintegrant was used in place of cross-linked polyvinyl

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pyrrolidone in compositions C and D.

[0129] The following results were obtained:

	Composition	% disintegration 10°C	% disintegration 20°C
A	5% PVP 22% acetate	100	100
B	3% PVP 24% acetate	97	100
C	5% PVP No acetate	100	100
D	3% PVP No acetate	81	91
A'	5% other polymer 22% acetate		less than 33
C'	5% cellulosic No acetate	56	53
D'	3% cellulosic No acetate	34	32

[0130] As can be seen from these results, cross-linked polyvinyl pyrrolidone was effective as a tablet disintegrant, even when sodium acetate was absent.

Example 3

[0131] Tablets for use in fabric washing were made, starting with granulated base powder of the following composition, made by mixing under high shear followed by densification under reduced shear in accordance with the procedure described in WO-A-98/11193.

Ingredient	Parts by Weight
Sodium linear alkylbenzene sulphonate	8.51
C ₁₃₋₁₅ fatty alcohol 7EO	2.44
C ₁₃₋₁₅ fatty alcohol 3EO	1.31
Soap	0.66
Maximum aluminium zeolite P	19.06
Sodium acetate trihydrate	2.41
Sodium carbonate (light soda ash)	2.82
Linear sodium carboxymethyl cellulose (SCMC)	0.38
Moisture and impurities	3.41
TOTAL	41.0

[0132] This powder was then mixed with further ingredients as follows in a low shear mixture for 5-20 seconds:

Ingredient	Parts by Weight
Base powder	41
Anti-foam granules	1.60
Fluorescer granules	1.50

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(continued)

Ingredient	Parts by Weight
Soil release polymer	1.00
Sodium citrate dihydrate	3.50
TAED granules	3.75
Sodium percarbonate (coated)	14.00
Sodium disilicate granules	3.00
Organic phosphonate sequestrants	1.22
Cross-linked polyvinyl pyrrolidone	5.00
Polyethylene glycol, molecular weight 6000	3.00
Sodium acetate trihydrate	21.00
Perfume	0.45
TOTAL	100

[0133] 40g portions of each composition were compacted into cylindrical tablets of 44 mm diameter and substantially equal tablet strength.

[0134] This procedure was carried out using various samples of cross-linked polyvinyl pyrrolidone, of different mean particle size.

[0135] Tablet disintegration, into water at 20°C, was tested as in the previous example. The results obtained were:

Mean Particle Size (micrometers)	% Disintegration
113µm	29%
174µm	33%
235µm	90%
253µm	100%
281µm	93%
396µm	100%

Claims

1. According to a first aspect of this invention, there is provided a tablet of a compacted particulate cleaning composition containing at least one cleaning ingredient which is an organic surfactant, a water softening agent or a bleach, wherein the tablet or a discrete region of the tablet contains 0.5% to 10% by weight of the tablet or region of disintegrant particles which contain cross-linked polyvinyl pyrrolidone.
2. A tablet according to claim 1 wherein the said disintegrant particles have a mean particle size greater than 250 micrometers and at least 70% of the disintegrant particles have size greater than 200 micrometers.
3. A tablet according to claim 1 or claim 2 wherein the disintegrant particles contain cross-linked polyvinyl pyrrolidone mixed with a carrier material.
4. A tablet according to claim 1 or claim 2 wherein the disintegrant particles contain more than 50% of cross-linked polyvinyl pyrrolidone.
5. A tablet according to any one of the preceding claims wherein the tablet or discrete region thereof is compacted from a composition which contains 20 to 99% by weight of particles which contain surfactant mixed with other ingredients, 1 to 10% by weight of said disintegrant particles, and 0 to 79% by weight of other particulate ingredients.

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6. A tablet according to claim 5 wherein the composition of the tablet or discrete region thereof contains from 35% to 55% of the surfactant-containing particles and these contain at least 90% of the organic surfactant in the composition.

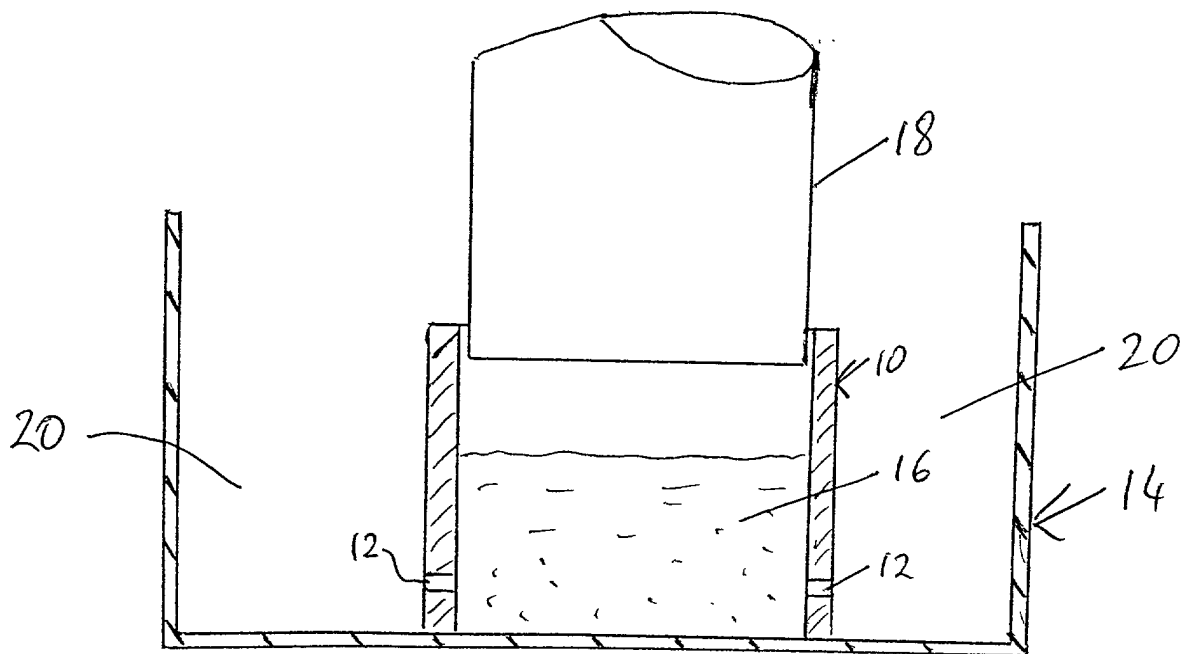
7. A tablet according to any one of the preceding claims wherein the tablet or discrete region thereof contains from 5 to 50% by weight of surfactant and from 5 to 80% by weight of water-softening agent.

8. A tablet according to any one of claims 1 to 6 wherein the tablet or a discrete region thereof contain from 0 to 5% by weight of surfactant, and either from 50 to 98% of water-softening agent or from 25 to 85% of a bleach.

9. A tablet according to any one of the preceding claims wherein the tablet or discrete region thereof also contains water-soluble disintegration-promoting particles containing at least 40% (by weight of the particles) of one or more materials selected from the group consisting of

- salts with 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.

10. A tablet according to claim 9 wherein the tablet or region thereof contain from 0 to 12% by weight of salt with a water-solubility exceeding 50gms per 100 gms water.





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Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 31 1743

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)
X	EP 1 036 839 A (BASF AG) 20 September 2000 (2000-09-20) * examples 1-4 *	1,2,4,5, 7,8	C11D17/00 C11D3/37 C11D3/39 C11D3/395
X	US 5 360 567 A (FRY ALAN J ET AL) 1 November 1994 (1994-11-01) * examples 2,3,6,10-13,15,16 *	1-5,7,8	
D,X	EP 0 522 766 A (UNILEVER PLC ;UNILEVER NV (NL)) 13 January 1993 (1993-01-13) * example 1 * * page 3, line 10 - line 16 *	1,2,5,7	
X	WO 00 43488 A (TCHEOU ERIC ;BINDER CHRISTOPHER JAMES (GB); LANT NEIL JOSEPH (GB);) 27 July 2000 (2000-07-27) * claims 1-10 *	1-4,10	
X	US 4 642 197 A (CARDUCK FRANZ-JOSEF ET AL) 10 February 1987 (1987-02-10) * column 6, line 18 - line 21 * * claims 1-6 *	1,3-5	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	DE 31 04 371 A (HENKEL KGAA) 11 November 1982 (1982-11-11) * page 4, line 4 - line 35 *	1,4-6,9	C11D
E	EP 1 074 608 A (MCBRIDE ROBERT LTD) 7 February 2001 (2001-02-07) * page 3, line 15 - line 16 * * claims 1-19 *	1,2,5	
D,A	WO 99 20730 A (UNILEVER PLC ;LEMPERS EDWIN LEO MARIO (NL); UNILEVER NV (NL); WAGN) 29 April 1999 (1999-04-29) * page 27, line 9 - line 13 * * claims 1-10 *	1-10	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 June 2001	Examiner Richards, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503-03.02 (P04001)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 31 1743

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 36493 A (RAMANAN GANAPATHY VENKATA ;KATSUDA RINKO (JP); INOUE TOMOTAKA (JP)) 22 July 1999 (1999-07-22) * claims 1-6 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 June 2001	Examiner Richards, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/02 (Rev.01)

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

EP 00 31 1743

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

14-06-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1036839 A	20-09-2000	DE 19912031 A	21-09-2000
		CN 1267715 A	27-09-2000
		JP 2000273490 A	03-10-2000
US 5360567 A	01-11-1994	AU 635141 B	11-03-1993
		AU 8030691 A	16-01-1992
		BR 9102951 A	11-02-1992
		CA 2046453 A,C	14-01-1992
		DE 69109192 D	01-06-1995
		DE 69109192 T	31-08-1995
		EP 0466484 A	15-01-1992
		ES 2071924 T	01-07-1995
		JP 2046192 C	25-04-1996
		JP 4253800 A	09-09-1992
		JP 7068557 B	26-07-1995
		KR 9504826 B	13-05-1995
		ZA 9105455 A	31-03-1993
EP 0522766 A	13-01-1993	AU 685384 B	22-01-1998
		AU 1937592 A	07-01-1993
		BR 9202449 A	16-03-1993
		CA 2072766 A	02-01-1993
		DE 69220147 D	10-07-1997
		DE 69220147 T	18-09-1997
		ES 2103891 T	01-10-1997
		JP 5186800 A	27-07-1993
		KR 9513227 B	26-10-1995
		US 5407594 A	18-04-1995
		ZA 9204891 A	03-01-1994
WO 0043488 A	27-07-2000	AU 2969100 A	07-08-2000
US 4642197 A	10-02-1987	DE 3417820 A	14-11-1985
		AT 36347 T	15-08-1988
		DE 3564286 D	15-09-1988
		EP 0170791 A	12-02-1986
		ES 543071 D	01-06-1986
		ES 8607382 A	01-11-1986
		JP 60252699 A	13-12-1985
DE 3104371 A	11-11-1982	NONE	
EP 1074608 A	07-02-2001	NONE	
WO 9920730 A	29-04-1999	AU 725525 B	12-10-2000
		AU 1030899 A	10-05-1999

EPO FORM P0459

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

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

EP 00 31 1743

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

14-06-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9920730 A		BR 9812955 A	08-08-2000
		CN 1276828 T	13-12-2000
		EP 1027421 A	16-08-2000
		HU 0004038 A	28-03-2001
		PL 340050 A	15-01-2001
		TR 200001042 T	21-08-2000
WO 9936493 A	22-07-1999	AU 5822798 A	02-08-1999
		BR 9814583 A	24-10-2000
		EP 1047759 A	02-11-2000

EPO FORM P0459

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