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(54) MULTI-PHASE SHAPED BODY WITH OPTIMIZED PHASE SPLIT

(57) This invention relates generally to cleaning tablets containing bleaching agent. More particularly, the invention relates to tablets, such as laundry detergent tablets, dishwashing detergent tablets, bleach tablets and water softening tablets, containing bleaching agent. In addition, two-phase or multi-phase cleaning tablets of compacted particulate detergent/cleaner comprising builder(s), bleaching agent, bleach activator(s) and optionally other ingredients of washing/cleaning compositions, wherein the bleach activator(s) is/are spatially separated from oxidation-sensitive substances in a demarcated region of the tablet.

Abstract

This invention relates generally to cleaning tablets containing bleaching agent. More particularly, the invention relates to tablets, such as laundry detergent tablets, dishwashing detergent tablets, bleach tablets and water softening tablets, containing bleaching agent. In addition, two-phase or multi-phase cleaning tablets of compacted particulate detergent/cleaner comprising builder(s), bleaching agent, bleach activator(s) and optionally other ingredients of washing/cleaning compositions, wherein the bleach activator(s) is/are spatially separated from oxidation-sensitive substances in a demarcated region of the tablet.

MULTI-PHASE SHAPED BODY WITH OPTIMIZED PHASE SPLIT

Field of the Invention

This invention relates generally to cleaning tablets containing bleaching agent. More particularly, the invention relates to tablets, such as laundry detergent tablets, dishwashing detergent tablets, bleach tablets and water softening tablets, containing bleaching agent.

Background of the Invention

Detergent compositions in the form of tablets have long been known and are widely described in the prior art although, hitherto, tablets have not been especially prominent on the market. The reason for this is that tablets, despite a number of advantages, also have disadvantages which have an adverse effect both on their production and use and on their acceptance by consumers. The main advantages of tablets, such as elimination of the need to measure out the quantity of product required by the consumer, the higher density and hence the reduced packaging and storage costs and an aesthetic aspect which should not be underestimated, are offset by such disadvantages as the dichotomy between acceptable hardness and sufficiently rapid disintegration and dissolution of the tablets and numerous technological difficulties in production and packaging.

A particular problem arises out of the incorporation of bleaching agents in cleaning tablets, particularly when, besides the bleaching agent, oxidation-sensitive active substances and auxiliaries are to be introduced into the tablets. As a result of the high density produced by heavy compression of the particulate premixes, substances incompatible with one another are in closer contact than is the case, for example, in a loose powder. The effect of this closer contact is that chemical incompatibilities between individual ingredients have a far more drastic effect than in conventional powder-form detergents.

Solutions proposed in the prior art for bleach-containing cleaning tablets seek to separate the bleaching agent from the other ingredients which could affect its stability. The separation of bleaching agent and bleach activator in particular has often been proposed as a solution.

Thus, European patent application **EP 481 792** (Unilever) describes detergent tablets containing a persalt and a bleach activator, the bleach activator having to have a certain pseudo-first-arrangement perhydrolysis constant. This document teaches that the bleaching agent should preferably be separated from bleach-destabilizing ingredients. If the bleaching agent is perborate and if a diacylated or polyacylated amine bleach activator is used, this measure is actually compulsory.

European patent application **EP 481 793** (Unilever) also describes detergent tablets. These detergent tablets contain sodium percarbonate as bleaching agent which is spatially separated from all those substances which can adversely affect its stability. This document also refers specifically to the separation of bleaching agent and bleach activator or substances which can be attacked by bleaching agents and, in the process, lead to a loss of bleaching activity.

European patent application **EP 395 333** (Unilever) describes tabletted detergent compositions containing sodium perborate and one or more substances from the group of diacylated or polyacylated amine bleach activators, enzymes and optical brighteners, the persalt not being separated from the substances of this group. The tablets disclosed in this application are stable and do not show any loss of bleaching agent or enzyme activity.

In the prior art literature, the problems of bleach stability and the stability of oxidation-sensitive ingredients in detergent tablets are attributed to the contact between bleaching agent and the ingredients in question. The separation of the bleaching agent from the bleach activator or from oxidation-sensitive ingredients is repeatedly proposed as a solution to the problem. None of the cited documents is concerned with other ways of simultaneously overcoming stability problems of oxidation-sensitive ingredients and the loss of activity of the bleaching agent in detergent tablets.

Now, the problem addressed by the present invention was to provide cleaning tablets which would overcome the problems mentioned. In particular, the stability problems of oxidation-sensitive ingredients such as, for example, dyes, optical brighteners, perfumes and enzymes would be overcome and the loss of activity of the bleaching agent, even over long periods, would be overcome.

Summary of the Invention

It has now been found that oxidation-sensitive substances are not oxidized and destroyed by contact with the bleaching agent, the bleaching agent losing activity in the process, instead the problems mentioned above are caused by contact between bleach activator and oxidation-sensitive substance.

Now, the present invention relates to two-phase or multi-phase cleaning tablets of compacted particulate detergent/cleaner comprising builder(s), bleaching agent, bleach activator(s) and optionally other ingredients of washing/cleaning compositions, in which the bleach activator(s) is/are present spatially separated from oxidation-sensitive substances in a demarcated region of the tablet.

The cleaning tablets according to the invention solve the problem of inadequate stability both of the bleaching agent and of the oxidation-sensitive substances through the spatial separation of oxidation-sensitive constituents, which are destroyed by the bleaching agent and can "consume" the bleaching agent in the process, from the bleach activator.

In the tablets according to the present invention, at least one spatially demarcated region contains the bleach activator and optionally other components which are not sensitive to oxidation. These non-oxidation-sensitive substances emanate, for example, from the group of builders, co-builders, surfactants, binders, disintegration aids and complexing agents and other optional ingredients of washing/cleanig compositions.

The spatial demarcation of the bleach activator can be achieved in various ways. Thus, the demarcated region may assume the form of a separate layer, a coating or individual inserts while the oxidation-sensitive substances may be present in other layers, in other coatings or in the core or the main matrix of the tablet. Another possibility is to produce comparatively large granules or extrudates which are protected by coating and which are distributed throughout the tablet.

In one preferred embodiment of the present invention, the demarcated region containing the bleach activator does not contain the bleach activator on its own, but rather in the form of a mixture with other non-oxidation-sensitive substances. Preferred cleaning tablets contain the bleach activator and other non-oxidation-sensitive ingredients of detergents/cleaners in the demarcated region.

In another preferred embodiment, the demarcated region contains the bleach activator and at least part of the total quantity of builders and ionic surfactants present in the tablet. Particularly preferred cleaning tablets have a demarcated region which, in addition to the bleach activator, contains one or more ingredients from the group of builders, co-builders, surfactants, binders, disintegration aids and complexing agents.

Without wishing in any way to be restricted by theory, applicants assume that the effect of separating the oxidation-sensitive substances from the bleach activator is that the penetration of water or hydrogen peroxide into the oxidation-sensitive substances in the absence of bleach activators does not lead to any drastic destruction of those compounds. If, by contrast, bleach activator and oxidation-sensitive substances are present in one and the same region, far more active bleaching species (for example peracetic acid) are formed from migrating H_2O or H_2O_2 under the influence of the bleach activator and lead to destruction of the oxidation-sensitive compounds. Since H_2O_2 is consumed in this way, more bleaching agent decomposes until an equilibrium concentration of H_2O_2 is re-established in the tablet. This process is prevented by the separation of bleach activator and oxidation-sensitive substances so that the bleach activator itself does not migrate in the tablet and even the more active bleaching species, which are formed by contact between bleach activator and H_2O_2, would appear to tend far less to migrate.

Detailed Description of the Invention

Preferred tablets are not produced from a mixture of individual powders, but at least partly from compounds, i.e. a mixture of a few granule types. The primary particles of the constituents are agglomerated to secondary particles which in turn are compressed to tablets. The secondary particles which contain the bleach activator are separated from oxidation-sensitive substances and, accordingly, are unable to contribute to the formation of highly bleaching species in the vicinity of the oxidation-sensitive substances.

Oxidation-sensitive substances in the context of the present invention are understood to be substances which can be oxidatively decomposed by H_2O_2 or compounds with a stronger bleaching effect formed from H_2O_2 and bleach activators. Such substances are, in particular, dyes which fade completely or unacceptably change color, optical brighteners where destruction of the molecule leads to loss of the brightening effect, perfumes which are oxidatively decomposed into odorless or even foul-smelling compounds and enzymes of which the oxidation products have no further catalytic activity.

Whereas oxidation-sensitive substances such as these are compulsorily separated from the bleach activator in accordance with the present invention through the presence of the bleach activator in a demarcated region of the tablets, the oxidation-sensitive substances may readily be present in close contact with the bleaching agent without suffering damage. Even the demarcated region containing the bleach activator may additionally contain bleaching agent, although according to the invention, the demarcated region (containing the bleach activator) is preferably free from bleaching agent(s).

The fact that the demarcated region (containing the bleach activator) is preferably free from bleaching agent does not mean that the bleaching agent has to be present in a demarcated region separated from substances other than the bleach activator. As explained above, the bleaching agent may readily be mixed with the oxidation-sensitive substances, so that cleaning tablets in which bleaching agent and oxidation-sensitive substance(s) are present together in one region of the tablets are preferred.

The essence of the present invention presupposes that the tablets contain oxidation-sensitive substances because their destruction and the resulting loss of activity from the bleaching agent are to be prevented. These oxidation-sensitive substances were explained in detail earlier on in the present specification, but may also be selected from other groups than those mentioned above. However, cleaning tablets which contain one or more substances from the group of dyes, optical brighteners, perfumes and enzymes as oxidation-sensitive substances are still preferred according to the present invention.

Bleach activators are incorporated in detergents in order to obtain an improved bleaching effect at washing temperatures of 60°C or lower. According to the invention, these bleach activators are present in a demarcated region of the tablets. Compounds which form aliphatic peroxocarboxylic acids preferably containing 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions may be used as bleach activators. Suitable bleach activators are substances which contain O- and/or N-acyl groups with the number of carbon atoms indicated and/or optionally substituted benzoyl groups. Preferred bleach activators are polyacylated alkylenediamines, more especially tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycol urils, more particularly tetraacetyl glycol uril (TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl- or isononanoyl-oxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more especially phthalic anhydride, acylated polyhydric alcohols, more especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

In addition to or instead of the conventional bleach activators, so-called bleach catalysts may also be incorporated in the tablets. Bleach catalysts are bleach-boosting transition metal salts or transition metal complexes such as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen complexes or carbonyl complexes. Mn-, Fe-, Co-, Ru-, Mo-, Ti-, V- and Cu-complexes with N-containing tripod ligands and Co-, Fe-, Cu- and Ru-ammine complexes may also be used as bleach catalysts.

According to the invention, bleach activators also include substances from the group of bleach catalysts, i.e. the bleach catalysts are also accommodated in the, or in a, demarcated region of the tablets. The tablets according to the invention contain between 0.5 and 30% by weight, preferably between 1 and 20% by weight and more preferably between 2 and 15% by weight, based on the tablet as a whole, of one or more bleach activators or bleach catalysts. These quantities may vary according to the application envisaged for the cleaning tablets. Thus, in typical heavy-duty detergent tablets, bleach activator contents of 0.5 to 5% by weight, preferably between 1 and 4% by weight and more preferably between 2 and 3.5% by weight are normal whereas bleach tablets contain much larger amounts, for example between 5 and 30% by weight, preferably between 7.5 and 25% by weight and more preferably between 10 and 20% by weight. The expert is not restricted in his freedom of formulation and can thus produce laundry detergent tablets, cleaner tablets or bleach tablets with a relatively strong or weak bleaching effect by varying the contents of bleach activator and bleaching agent.

A particularly preferred bleach activator is N,N,N',N'-tetraacetyl ethylenediamine which is widely used in detergents. Accordingly, preferred cleaning tablets are characterized in that tetraacetyl ethylenediamine in the quantities mentioned above is used as bleach activator.

To develop the required bleaching performance, the cleaning tablets according to the invention contain one or more bleaching agents. Among the compounds yielding H_2O_2 in water which serve as bleaching agents, sodium perborate tetrahydrate and sodium perborate monohydrate are particularly important. Other useful bleaching agents are, for example, sodium percarbonate, peroxypyrophosphates, citrate perhydrates and H_2O_2-yielding peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecane dioic acid. The bleaching agents are also used in varying quantities in the cleaning tables according to the invention, depending on the desired product. Typical contents are between 5 and 50% by weight, preferably between 10 and 40% by weight and more preferably between 15 and 35% by weight, based on the tablet as a whole. The content of bleaching agents in the tablets is again dependent on the application envisaged for the tablets. Whereas typical heavy-duty detergents in tablet form contain between 5 and 30% by weight, preferably between 7.5 and 25% by weight and more preferably between 12.5 and 22.5% by weight of bleaching agent, bleach or bleach booster tablets contain between 15 and 50% by weight, preferably between 22.5 and 45% by weight and more preferably between 30 and 40% by weight of bleaching agent.

As explained above, the oxidation-sensitive substances preferably emanate from the group of dyes, optical brighteners, perfumes and enzymes. These groups are described in more detail in the following.

In order to improve their aesthetic impression, the cleaning tablets according to the invention may be colored with suitable dyes. Preferred dyes, which are not difficult for the expert to choose, have high stability in storage, are not affected by the other ingredients of the detergents or by light and do not have any pronounced substantivity for textile fibers so as not to color them. Since the present invention relates to multi-phase cleaning tablets, considerable significance attaches to the coloring of individual phases in order to underscore the differences in active character between individual phases. Examples of the effectiveness of such coloring and of the success of relevant claims are sufficiently known from the advertising of denture cleaning preparations.

Any dyes which can be destroyed by oxidation in the washing process and mixtures thereof with suitable blue dyes, so-called blueing agents, are preferably used in the cleaning tablets according to the invention. It has proved to be of advantage to use dyes which are soluble in water or - at room temperature - in liquid organic substances. Suitable dyes are, for example, anionic dyes, for example anionic nitroso dyes. One possible dye is, for example, naphthol green (Color Index (CI) Part 1: Acid Green 1; Part 2: 10020), which is commercially available for example as Basacid® Grün 970 from BASF, Ludwigshafen, and mixtures thereof with suitable blue dyes. Other suitable dyes are Pigmosol® Blau 6900 (CI

74160), Pigmosol® Grün 8730 (CI 74260), Basonyl® Rot 545 FL (CI 45170), Sandolan® Rhodamin EB 400 (CI 45100), Basacid® Gelb 094 (CI 47005), Sicovit® Patentblau 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol® Blau GLW (CAS 12219-32-8, CI Acid Blue 221), Nylosan® Gelb N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan® Blau (CI Acid Blue 182, CAS 12219-26-0).

In selecting the dye, it is important to ensure that the dye does not have an excessive affinity for the textile surfaces and, in particular, for synthetic fibers. Another factor to be taken into account in the selection of suitable dyes is that dyes differ in their stability to oxidation. Generally speaking, water-insoluble dyes are more stable to oxidation than water-soluble dyes. The concentration of the dye in the detergents varies according to its solubility and hence its sensitivity to oxidation. In the case of readily water-soluble dyes, for example the above-mentioned Basacid® Grün and Sandolan® Blau, dye concentrations in the range from a few 10^{-2} to 10^{-3} % by weight are typically selected. By contrast, in the case of the pigment dyes which are particularly preferred for their brilliance, but which are less readily soluble in water, for example the above-mentioned Pigmosol® dyes, suitable concentrations of the dye in cleaners or laundry detergents are typically of the order of a few 10^{-3} to 10^{-4} % by weight.

The tablets may contain optical brighteners selected from derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as oxidation-sensitive substances. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar composition which contain a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-

bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned above may also be used. The optical brighteners are used in the cleaning tablets according to the invention in concentrations of 0.01 to1% by weight, preferably in concentrations of 0.05 to 0.5% by weight and more preferably in concentrations of 0.1 to 0.25% by weight, based on the tablet as a whole.

Perfumes are added to the cleaning tablets according to the invention to improve the aesthetic impression created by the products and to provide the consumer not only with the required washing performance but also with a visually and sensorially "typical and unmistakable" product. Suitable perfume oils or fragrances include individual perfume compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Perfume compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexyl acetate, linalyl acetate, dimethyl benzyl carbinyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethyl methyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α-isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol and the hydrocarbons include, above all, the terpenes, such as limonene and pinene. However, mixtures of various perfumes which together produce an attractive perfume note are preferably used. Perfume oils such as these may also contain natural perfume mixtures obtainable from vegetable sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are clary oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

The perfume content of the cleaning tablets according to the invention is normally up to 2% by weight of the formulation as a whole. The perfumes may be directly incorporated in the tablets according to the invention, although it can also be of advantage to apply the perfumes to supports which strengthen the adherence of the perfume to the washing and which provide the textiles with a long-lasting fragrance through a slower release of the perfume. Suitable support materials are, for example, cyclodextrins, the cyclodextrin/perfume complexes optionally being coated with other auxiliaries.

Suitable enzymes are those from the class of proteases, lipases, amylases, cellulases or mixtures thereof. Enzymes obtained from bacterial strains or fungi, such as Bacillus subtilis, Bacillus licheniformis and Streptomyces griseus, are particularly suitable. Proteases of the subtilisin type are preferred, proteases obtained from Bacillus lentus being particularly preferred. Enzyme mixtures, for example of protease and amylase or protease and lipase or protease and cellulase or of cellulase and lipase or of protease, amylase and lipase or of protease, lipase and cellulase, but especially cellulase-containing mixtures, are of particular interest. Peroxidases or oxidases have also proved to be suitable in some cases. The enzymes may be adsorbed to supports and/or encapsulated in membrane materials to protect them against premature decomposition. The percentage content of the enzymes, enzyme mixtures or enzyme granules in the tablets according to the invention may be, for example, from about 0.1 to 5% by weight and is preferably from 0.1 to about 2% by weight.

In the context of the present invention, "spatial separation" means that the separate layer, coating or individual insert containing the bleach activator is completely free from the oxidation-sensitive substances mentioned. As already mentioned in the foregoing, this can be achieved, for example, by producing separate secondary granules which, apart from the bleach activator, contain only non-oxidation-sensitive substances and tabletting these secondary granules after mixing with other constituents and/or compounds. The production of a two-layer or multi-layer tablet in which only one layer contains bleach activator is also possible. In this case, oxidation-sensitive substances may be used in (one of) the other layer(s). In a preferred embodiment of the present invention, the demarcated region of the tablets assumes the form of a separate layer, a coating or individual inserts, multi-layer tablets being particularly preferred. Thus, the individual phases of the tablet according to the invention may assume different three-dimensional forms. As already mentioned, the most simple form is a two-layer or multi-layer tablet in which each layer of the tablet represents a phase. However, it is also possible in accordance with the invention to produce multi-phase tablets in which individual phases assume the form of inclusions in (one of the) other phase(s). Besides so-called "ring/core tablets", jacket tablets or combinations of the embodiments mentioned, for example, are possible. Examples of multi-phase tablets can be found in the drawings of **EP-A-0 055 100** (Jeyes) which describes lavatory cleaning blocks. At present, the most widespread form of multi-phase tablets is the two-layer or multi-layer tablet.

Besides the ingredients mentioned, the cleaning tablets according to the invention may contain other ingredients in quantities determined by the application envisaged for the tablets. Thus, substances from the group of surfactants, builders and polymers are particularly suitable for use in the cleaning tablets according to the invention. The expert will again have no difficulty in selecting the individual components and the quantities in which to use them. For example, a heavy-duty detergent tablet will contain relatively large quantities of surfactant(s) whereas a bleaching tablet may even contain no surfactant at all. The quantity of builder(s) used also varies according to the intended application.

The cleaning tablets according to the invention may contain any of the builders typically used in detergents and cleaners, i.e. in particular zeolites, silicates, carbonates, organic cobuilders and - providing there are no ecological objections to their use - also the phosphates.

Suitable crystalline layered sodium silicates correspond to the general formula $NaMSi_xO_{2x+1}y\ H_2O$, where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layered silicates such as these are described, for example, in European patent application **EP-A-0 164 514**. Preferred crystalline layered silicates corresponding to the above formula are those in which M is sodium and x assumes the value 2 or 3. Both β- and δ-sodium disilicates $Na_2Si_2O_5y\ H_2O$ are particularly preferred, β-sodium disilicate being obtainable, for example, by the process described in International patent application **WO-A- 91/08171**.

Other useful builders are amorphous sodium silicates with a modulus ($Na_2O:SiO_2$ ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more preferably 1:2 to 1:2.6 which dissolve with delay and exhibit multiple wash cycle properties. The delay in dissolution in relation to conventional amorphous sodium silicates can have been obtained in various ways, for example by surface treatment, compounding, compacting or by overdrying. In the context of the invention, the term “amorphous” is also understood to encompass “X-ray amorphous”. In other words, the silicates do not produce any of the sharp X-ray reflexes typical of crystalline substances in X-ray diffraction experiments, but at best one or more maxima of the scattered X-radiation which have a width of several degrees of the diffraction angle. However, particularly good builder properties may even be achieved where the silicate particles produce crooked or even sharp diffraction maxima in electron diffraction experiments. This may be interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and, more particularly, up to at most 20 nm being preferred. So-called X-ray amorphous silicates such as these, which also dissolve with delay in relation to conventional waterglasses, are described for example in German patent application **DE-A-44 00 024**. Compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are particularly preferred.

The finely crystalline, synthetic zeolite containing bound water used in accordance with the invention is preferably zeolite A and/or zeolite P. Zeolite MAP® (Crosfield) is a particularly preferred P-type zeolite. However, zeolite X and mixtures of A, X and/or P are also suitable. According to the invention, it is preferred to use, for example, a commercially obtainable co-crystallizate of zeolite X and zeolite A (ca. 80% by weight zeolite X) which is marketed by CONDEA Augusta S.p.A. under the name of VEGOBOND AX® and which may be described by the following formula:

$$n\mathrm{Na_2O} \cdot (1\text{-}n)\mathrm{K_2O} \cdot \mathrm{Al_2O_3} \cdot (2 - 2.5)\mathrm{SiO_2} \cdot (3.5 - 5.5)\ \mathrm{H_2O}.$$

The zeolite may be used both as a builder in a granular compound and for "powdering" the entire mixture to be tabletted, both these options normally being used to incorporate the zeolite in the premix. Suitable zeolites have a mean particle size of less than 10 μm (volume distribution, as measured by the Coulter Counter Method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water.

The generally known phosphates may of course also be used as builders providing their use should not be avoided on ecological grounds. The sodium salts of the orthophosphates, the pyrophosphates and especially the tripolyphosphates are particularly suitable.

The quantity of builder is normally between 10 and 70% by weight, preferably between 15 and 60% by weight and more preferably between 20 and 50% by weight. The quantity of builders used is again dependent on the intended application so that bleach tablets can contain larger quantities of builders (for example between 20 and 70% by weight, preferably between 25 and 65% by weight and more preferably between 30 and 55% by weight) than, for example, detergent tablets (normally 10 to 50% by weight, preferably 12.5 to 45% by weight and more preferably between 17.5 and 37.5% by weight).

Useful organic builders are, for example, the polycarboxylic acids usable, for example, in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, benzene hexacarboxylic acid, sugar acids, for example gluconic acid, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing its use is not ecologically unsafe, and mixtures thereof. Preferred salts are the salts of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

Anionic, nonionic, cationic and/or amphoteric surfactants and mixtures thereof may be used in the cleaning tablets according to the invention. Mixtures of anionic and nonionic surfactants are preferred from the performance perspective. The total surfactant content of the tablets is between 5 and 60% by weight, based on tablet weight, surfactant contents above 15% by weight being preferred.

Suitable anionic surfactants are, for example, those of the sulfonate and sulfate type. Suitable surfactants of the sulfonate type are preferably C_{9-13} alkyl benzenesulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxyalkane sulfonates, and the disulfonates obtained, for example, from C_{12-18} monoolefins with an internal or terminal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Other suitable surfactants of the sulfonate type are the alkane sulfonates obtained from C_{12-18} alkanes, for example by sulfochlorination or sulfoxidation and subsequent hydrolysis or neutralization. The esters of α-sulfofatty acids (ester sulfonates), for example the α-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids, are also suitable.

Other suitable anionic surfactants are sulfonated fatty acid glycerol esters. Fatty acid glycerol esters in the context of the present invention are the monoesters, diesters and triesters and mixtures thereof which are obtained where production is carried out by esterification of a monoglycerol with 1 to 3 moles of fatty acid or in the transesterification of triglycerides with 0.3 to 2 moles of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated fatty acids containing 6 to 22 carbon atoms, for example caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

Preferred alk(en)yl sulfates are the alkali metal salts and, in particular, the sodium salts of the sulfuric acid semiesters of C_{12-18} fatty alcohols, for example coconut alcohol, tallow alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or C_{10-20} oxoalcohols and the corresponding semiesters of secondary alcohols with the same chain length. Other preferred alk(en)yl sulfates are those with the chain length mentioned which contain a synthetic, linear alkyl chain based on a petrochemical and which are similar in their degradation behavior to the corresponding compounds based on oleochemical raw materials. C_{12-16} alkyl sulfates, C_{12-15} alkyl sulfates and C_{14-15} alkyl sulfates are preferred from the point of view of washing technology. Other suitable anionic surfactants are 2,3-alkyl sulfates which may be produced, for example, in accordance with **US 3,234,258** or **US 5,075,041** and which are commercially obtainable as products of the Shell Oil Company under the name of DAN®.

The sulfuric acid monoesters of linear or branched C_{7-21} alcohols ethoxylated with 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C_{9-11} alcohols containing on average 3.5 moles of ethylene oxide (EO) or C_{12-18} fatty alcohols containing 1 to 4 EO, are also suitable. In view of their high foaming capacity, they are only used in relatively small quantities, for example in quantities of 1 to 5% by weight, in dishwashing detergents.

Other suitable anionic surfactants are the salts of alkyl sulfosuccinic acid which are also known as sulfosuccinates or as sulfosuccinic acid esters and which represent monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and, more particularly, ethoxylated fatty alcohols. Preferred sulfosuccinates contain C_{8-18} fatty alcohol residues or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol residue derived from ethoxylated fatty alcohols which, considered in isolation, represent nonionic surfactants (for a description, see below). Of these sulfosuccinates, those of which the fatty alcohol residues are derived from narrow-range ethoxylated fatty alcohols are particularly preferred. Alk(en)yl succinic acid preferably containing 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof may also be used.

Other suitable anionic surfactants are, in particular, soaps. Suitable soaps are saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and soap mixtures derived in particular from natural fatty acids, for example coconut oil, palm kernel oil or tallow fatty acids.

The anionic surfactants, including the soaps, may be present in the form of their sodium, potassium or ammonium salts and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably present in the form of their sodium or potassium salts and, more preferably, in the form of their sodium salts.

Preferred nonionic surfactants are alkoxylated, advantageously ethoxylated, more especially primary alcohols preferably containing 8 to 18 carbon atoms and, on average, 1 to 12 moles of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in the 2-position or may contain linear and methyl-branched radicals in the form of the mixtures typically present in oxoalcohol radicals. However, alcohol ethoxylates containing linear radicals of alcohols of native origin with 12 to 18 carbon atoms, for example coconut oil, palm oil, tallow or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C_{12-14} alcohols containing 3 EO or 4 EO, C_{9-11} alcohol containing 7 EO, C_{13-15} alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols containing 3 EO, 5 EO or 7 EO and mixtures thereof, such as mixtures of C_{12-14} alcohol containing 3 EO and C_{12-18} alcohol containing 5 EO. The degrees of ethoxylation mentioned represent statistical mean values which, for a special product, can be a whole number or a broken number. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, fatty alcohols containing more than 12 EO may also be used, examples including tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

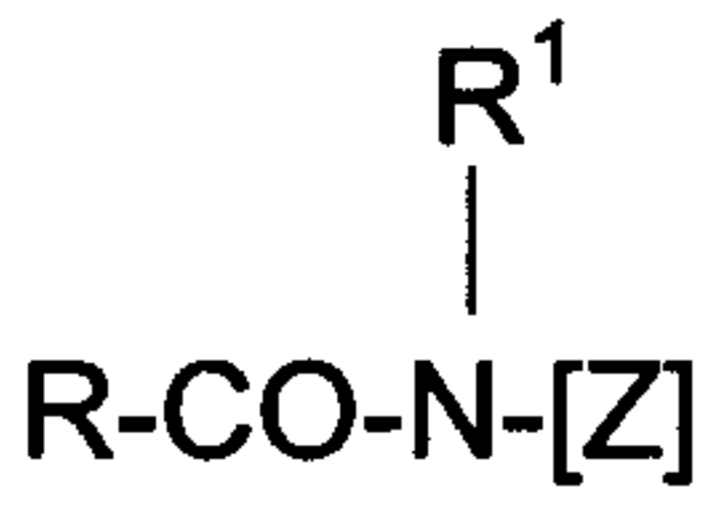
In addition, alkyl glycosides corresponding to the general formula $RO(G)_x$ where R is a primary linear or branched, more particularly 2-methyl-branched, aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glycose unit containing 5 or 6 carbon atoms, preferably glucose, may be used as further nonionic surfacants.

The degree of oligomerization x, which indicates the distribution of monoglycosides and oligoglycosides, is a number between 1 and 10; x preferably has a value of 1.2 to 1.4.

Another class of preferred nonionic surfactants which may be used either as sole nonionic surfactant or in combination with other nonionic surfactants are alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters preferably containing 1 to 4 carbon atoms in the alkyl chain, more especially the fatty acid methyl esters which are described, for example, in Japanese patent application **JP 58/217598** or which are preferably produced by the process described in International patent application **WO-A-90/13533**.

Nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and the fatty acid alkanolamide type are also suitable. The quantity in which these nonionic surfactants are used is preferably no more than the quantity in which the ethoxylated fatty alcohols are used and, more preferably, no more than half that quantity.

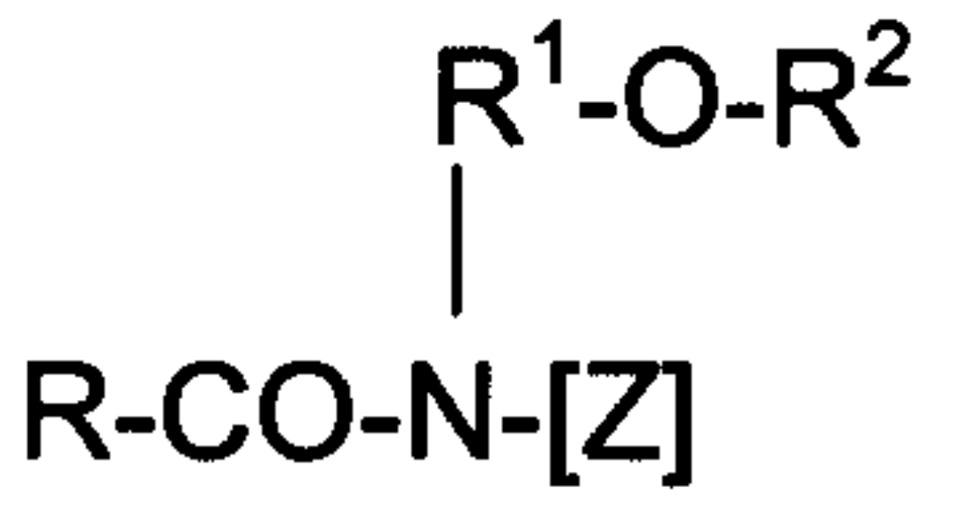
Other suitable surfactants are polyhydroxyfatty acid amides corresponding to formula (I):



$$\text{R-CO-}\overset{\displaystyle R^1}{\overset{|}{\text{N}}}\text{-[Z]} \qquad \text{(I)}$$

in which RCO is an aliphatic acyl group containing 6 to 22 carbon atoms, R^1 is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl group containing 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxyfatty acid amides are known substances which may normally be obtained by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of polyhydroxyfatty acid amides also includes compounds corresponding to formula (II):



$$\mathrm{R\text{-}CO\text{-}}\overset{\displaystyle \mathrm{R^1\text{-}O\text{-}R^2}}{\overset{|}{\mathrm{N}}}\mathrm{\text{-}[Z]} \qquad \mathrm{(II)}$$

in which R is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl group or an aryl group containing 2 to 8 carbon atoms and R^2 is a linear, branched or cyclic alkyl group or an aryl group or an oxyalkyl group containing 1 to 8 carbon atoms, C_{1-4} alkyl or phenyl groups being preferred, and [Z] is a linear polyhydroxyalkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of that group.

[Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds may then be converted into the required polyhydroxyfatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example in accordance with the teaching of International patent application **WO-A-95/07331**.

According to the invention, preferred cleaning tablets are those containing anionic and nonionic surfactant(s). Performance-related advantages can arise out of certain quantity ratios in which the individual classes of surfactants are used.

For example, particularly preferred cleaning tablets are characterized in that the ratio of anionic surfactant(s) to nonionic surfactant(s) is from 10:1 to 1:10, preferably from 7.5:1 to 1:5 and more preferably from 5:1 to 1:2.

It can be of advantage from the performance point of view if certain classes of surfactants are missing from certain phases of the cleaning tablets or from the entire tablet, i.e. from every phase. In another important embodiment of the present invention, therefore, at least one phase of the cleaning tablets is free from nonionic surfactants.

Conversely, a positive effect can also be obtained through the presence of certain surfactants in individual phases or in the cleaning tablet as a whole, i.e. in every phase. Introducing the alkyl polyglycosides described above has proved to be of particular advantage, so that cleaning tablets in which at least one phase of the tablet contains alkyl polyglycosides are preferred.

As with the nonionic surfactants, the omission of anionic surfactants from individual phases or from all phases can result in cleaning tablets which are more suitable for certain applications. Accordingly, cleaning tablets where at least one phase of the tablet is free from anionic surfactants are also possible in accordance with the present invention.

In order to facilitate the disintegration of heavily cleaning compacted tablets, disintegration aids, so-called tablet disintegrators, may be incorporated in them to shorten their disintegration times. According to **Römpp (9th Edition, Vol. 6, page 4440)** and **Voigt *"Lehrbuch der pharmazeutischen Technologie"* (6th Edition, 1987, pages 182-184)**, tablet disintegrators or disintegration accelerators are auxiliaries which promote the rapid disintegration of tablets in water or gastric juices and the release of the pharmaceuticals in an absorbable form.

These substances, which are also known as "disintegrators" by virtue of their effect, are capable of undergoing an increase in volume on contact with water so that, on the one hand, their own volume is increased (swelling) and, on the other hand, a pressure can be generated through the release of gases which causes the tablet to disintegrate into relatively small particles. Well-known disintegration aids are carbonate/citric acid systems, although other organic acids may also be used. Swelling disintegration aids are, for example, synthetic polymers, such as polyvinyl pyrrolidone (PVP), or natural polymers and modified natural substances, such as cellulose and starch and derivatives thereof, alginates or casein derivatives.

Preferred cleaning tablets contain 0.5 to 10% by weight, preferably 3 to 7% by weight and more preferably 4 to 6% by weight of one or more disintegration aids, based on tablet weight.

According to the invention, preferred disintegrators are cellulose-based disintegrators, so that preferred cleaning tablets contain a cellulose-based disintegrator in quantities of 0.5 to 10% by weight, preferably 3 to 7% by weight and more preferably 4 to 6% by weight. Pure cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, formally, is a β-1,4-polyacetal of cellobiose which, in turn, is made up of two molecules of glucose. Suitable celluloses consist of ca. 500 to 5000 glucose units and, accordingly, have average molecular weights of 50,000 to 500,000. According to the invention, cellulose derivatives obtainable from cellulose by polymer-analog reactions may also be used as cellulose-based disintegrators. These chemically modified celluloses include, for example, products of esterification or etherification reactions in which hydroxy hydrogen atoms have been substituted. However, celluloses in which the hydroxy groups have been replaced by functional groups that are not attached by an oxygen atom may also be used as cellulose derivatives. The group of cellulose derivatives includes, for example, alkali metal celluloses, carboxymethyl cellulose (CMC), cellulose esters and ethers and aminocelluloses. The cellulose derivatives mentioned are preferably not used on their own, but rather in the form of a mixture with cellulose as cellulose-based disintegrators. The content of cellulose derivatives in mixtures such as these is preferably below 50% by weight and more preferably below 20% by weight, based on the cellulose-based disintegrator. In one particularly preferred embodiment, pure cellulose free from cellulose derivatives is used as the cellulose-based disintegrator.

The cellulose used as disintegration aid is preferably not used in fine-particle form, but is converted into a coarser form, for example by granulation or compacting, before it is added to and mixed with the premixes to be tabletted. Detergent tablets which contain granular or optionally co-granulated disintegrators are described in German patent applications **DE 197 09 991** (Stefan Herzog) and **DE 197 10 254** (Henkel) and in International patent application **PCT/EP98/01203** (Henkel). Further particulars of the production of granulated, compacted or co-granulated cellulose disintegrators can also be found in these patent applications. The particle sizes of such disintegration aids are mostly above 200 µm, preferably at least 90% by weight of the particles being between 300 and 1600 µm in size and, more particularly, between 400 and 1200 µm in size. According to the invention, the above-described relatively coarse-particle cellulose-based disintegrators described in detail in the cited patent applications are preferably used as disintegration aids and are commercially obtainable, for example under the name of Arbocel® TF-30-HG from Rettenmaier.

Microcrystalline cellulose may be used as another cellulose-based disintegration aid or as part of such a component. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which only attack and completely dissolve the amorphous regions (ca. 30% of the total cellulose mass) of the celluloses, but leave the crystalline regions (ca. 70%) undamaged. Subsequent de-aggregation of the microfine celluloses formed by hydrolysis provides the microcrystalline celluloses which have primary particle sizes of ca. 5 µm and which can be compacted, for example, to granules with a mean particle size of 200 µm.

Cleaning tablets additionally containing a disintegration aid preferably based on cellulose, preferably in granular, cogranulated or compacted form, in quantities of 0.5 to 10% by weight, preferably in quantities of 3 to 7% by weight and more preferably in quantities of 4 to 6% by weight, based on tablet weight, represent a particularly preferred embodiment of the invention.

Besides the constituents mentioned - bleach activator, bleaching agent, oxidation-sensitive substance, surfactant, builder and disintegration aid - the cleaning tablets according to the invention may contain other typical ingredients of washing/cleaning compositions from the group of foam inhibitors, silicone oils, redeposition inhibitors, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

In addition, the cleaning tablets according to the invention may also contain components with a positive effect on the removal of oil and fats from textiles by washing (so-called soil repellents). This effect becomes particularly clear when a textile which has already been repeatedly washed with a detergent according to the invention containing this oil- and fat-dissolving component is soiled. Preferred oil- and fat-dissolving components include, for example, nonionic cellulose ethers, such as methyl cellulose and methyl hydroxypropyl cellulose containing 15 to 30% by weight of methoxyl groups and 1 to 15% by weight of hydroxypropoxyl groups, based on the nonionic cellulose ether, and the polymers of phthalic acid and/or terephthalic acid known from the prior art or derivatives thereof, more particularly polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Of these, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are particularly preferred.

Cleaning tablets are produced by the application of pressure to a mixture to be tabletted which is accommodated in the cavity of a press. In the most simple method of tablet production – hereinafter referred to simply as tabletting – the mixture to be tabletted is compressed directly, i.e. without preliminary granulation. The advantages of this so-called direct tabletting are its simple and inexpensive application because no other process steps and hence no other items of equipment are involved. However, these advantages are offset by disadvantages. Thus, a powder mixture which is to be directly tabletted must possess adequate plastic deformability and good flow properties and must not show any tendency to separate during storage, transportation and filling of the die. Unfortunately, these three requirements are very difficult to satisfy with many mixtures so that direct tabletting is often not applied, particularly in the production of cleaning tablets. Accordingly, the normal method of producing detergent tablets starts out from powder-form components ("primary particles") which are agglomerated or granulated by suitable methods to secondary particles with larger particle diameters. These granules or mixtures of different granules are then mixed with individual powder-form additives and the resulting mixtures are tabletted. Depending on the composition of the phases of the multi-phase detergent tablets, the die is filled in steps with different premixes. In the production of multi-layer tablets, the application of light pressure between the fillings with premixes can have advantages for the next step. In the production of ring/core tablets or jacket tablets, precompression and shaping/forming such as this is even almost indispensable.

According to the invention, preferred cleaning tablets are obtained by tabletting particulate premixes of at least one batch of surfactant-containing granules and at least one subsequently added powder-form component. The surfactant-containing granules may be produced by conventional granulation processes, such as mixer and pan granulation, fluidized bed granulation, extrusion, pelleting or compacting. It is of advantage so far as the subsequent detergent tablets are concerned if the premixes to be tabletted have a bulk density approaching that of standard compact detergents. In one particularly preferred embodiment, the premix to be tabletted has a bulk density of at least 500 g/l, preferably of at least 600 g/l and more preferably above 700 g/l. Another advantage can arise out of a relatively narrow particle size distribution of the surfactant granules used. According to the invention, preferred cleaning tablets are those in which the granules have particle sizes of 10 to 4,000 µm, preferably between 100 and 2,000 µm and more preferably between 600 and 1,400 µm.

Before the particulate premix is compressed to form detergent tablets, it may be "powdered" with fine-particle surface treatment materials. This can be of advantage to the quality and physical properties of both the premix (storage, tabletting) and the final cleaning tablets. Fine-particle powdering materials have been known for some time in the art, zeolites, silicates and other inorganic salts generally being used. However, the premix is preferably "powdered" with fine-particle zeolite, zeolites of the faujasite type being preferred. In the context of the present invention, the expression "zeolite of the faujasite type" encompasses all three zeolites which form the faujasite subgroup of zeolite structural group 4 (cf. Donald W. Breck: **"Zeolite Molecular Sieves"** John Wiley & Sons, New York/London/Sydney/Toronto, 1974, page 92). Besides zeolite X, therefore, zeolite Y and faujasite and mixtures of these compounds may also be used, pure zeolite X being preferred.

Mixtures or co-crystallizates of faujasite zeolites with other zeolites, which do not have to belong to zeolite structural group 4, may also be used for powdering, in which case at least 50% by weight of the powdering material advantageously consists of a zeolite of the faujasite type.

According to the invention, preferred cleaning tablets consist of a particulate premix containing granular components and subsequently incorporated powder-form components, the, or one of the, fine-particle components subsequently incorporated being a zeolite of the faujasite type with particle sizes below 100 µm, preferably below 10 µm and more preferably below 5 µm and making up at least 0.2% by weight, preferably at least 0.5% by weight and more preferably more than 1% by weight of the premix to be compressed.

The fine-particle aftertreatment components with the particle sizes mentioned above may be dry-mixed with the premix to be tabletted. However, it is also possible and preferred to "stick" them onto the surface of the relatively coarse particles by addition of small quantities of liquid components. These powdering techniques are widely described in the prior art literature and familiar to the expert. Liquid components suitable as adhesion promoters for the powdering materials are, for example, nonionic surfactants or aqueous solutions of surfactants or other detergent ingredients. In one preferred embodiment of the invention, perfume is used as the liquid component for promoting adhesion between the powdering materials and the coarse particles.

The cleaning tablets according to the invention are produced by first dry mixing the constituents of the individual phases, which may be completely or partly pregranulated, and then forming/shaping, more particularly tabletting, the resulting mixtures using conventional processes. To produce the multi-phase tablets according to the invention, the premixes are compacted between two punches in a die to form a solid compactate. This process, which is referred to in short hereinafter as tabletting, comprises four phases, namely metering, compacting (elastic deformation), plastic deformation and ejection.

The tabletting process is carried out in commercially available tablet presses which, in principle, may be equipped with single or double punches. In the latter case, not only is the top punch used to build up pressure, the bottom punch also moves towards the top punch during the tabletting process while the top punch presses downwards. For small production volumes, it is preferred to use eccentric tablet presses in which the punch(es) is/are fixed to an eccentric disc which, in turn, is mounted on a shaft rotating at a certain speed. The movement of these punches is comparable with the operation of a conventional four-stroke engine. Tabletting can be carried out with a top punch and a bottom punch, although several punches can also be fixed to a single eccentric disc, in which case the number of die bores is correspondingly increased. The throughputs of eccentric presses vary according to type from a few hundred to at most 3,000 tablets per hour.

For larger throughputs, rotary tablet presses are generally used. In rotary tablet presses, a relatively large number of dies is arranged in a circle on a so-called die table. The number of dies varies – according to model – between 6 and 55, although even larger dies are commercially available. Top and bottom punches are associated with each die on the die table, the tabletting pressures again being actively built up not only by the top punch or bottom punch, but also by both punches. The die table and the punches move about a common vertical axis, the punches being brought into the filling, compaction, plastic deformation and ejection positions by means of curved guide rails. At those places where the punches have to be raised or lowered to a particularly significant extent (filling, compaction, ejection), these curved guide rails are supported by additional push-down members, pull-down rails and ejection paths. The die is filled from a rigidly arranged feed unit, the so-called filling shoe, which is connected to a storage container for the compound. The pressure applied to the premix can be individually adjusted through the tools for the top and bottom punches, pressure being built up by the rolling of the punch shank heads past adjustable pressure rollers.

To increase throughput, rotary presses can also be equipped with two filling shoes so that only half a circle has to be negotiated to produce a tablet. To produce two-layer or multi-layer tablets, several filling shoes are arranged one behind the other without the lightly compacted first layer being ejected before further filling. Given suitable process control, shell and bull's-eye tablets – which have a structure resembling an onion skin – can also be produced in this way. In the case of bull's-eye tablets, the upper surface of the core or rather the core layers is not covered and thus remains visible. Rotary tablet presses can also be equipped with single or multiple punches so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be simultaneously used for tabletting. Modern rotary tablet presses have throughputs of more than one million tablets per hour.

Tabletting machines suitable for step a) of the process according to the invention can be obtained, for example, from the following companies: Apparatebau Holzwarth GbR, Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen GmbH, Berlin, Mapag Maschinenbau AG, Bern (Switzerland) and Courtoy N.V., Halle (BE/LU). One example of a particularly suitable tabletting machine is the model HPF 630 hydraulic double-pressure press manufactured by LAEIS, D.

The tablets can be made in certain shapes and certain sizes and may also consist of several phases, i.e. layers, inclusions or cores and rings. Suitable shapes are virtually any easy-to-handle shapes, for example slabs, bars, cubes, squares and corresponding shapes with flat sides and, in particular, cylindrical forms of circular or oval cross-section. This last embodiment encompasses shapes from tablets to compact cylinders with a height-to-diameter ratio of more than 1.

The portioned pressings may be formed as separate individual elements which correspond to a predetermined dose of the detergent/cleaner. However, it is also possible to form pressings which combine several such units in a single pressing, smaller portioned units being easy to break off in particular through the provision of predetermined weak spots. For the use of laundry detergents in machines of the standard European type with horizontally arranged mechanics, it can be of advantage to produce the portioned pressings as cylindrical or square tablets, preferably with a diameter-to-height ratio of about 0.5:2 to 2:0.5. Commercially available hydraulic presses, eccentric presses and rotary presses are particularly suitable for the production of pressings such as these.

The three-dimensional form of another embodiment of the tablets is adapted in its dimensions to the dispensing compartment of commercially available domestic washing machines, so that the tablets can be introduced directly, i.e. without a dosing aid, into the dispensing compartment where they dissolve on contact with water. The cleaning tablets may of course also be used in conjunction with a dosing aid.

Another preferred multi-phase tablet which can be produced has a plate-like or slab-like structure with alternately thick long segments and thin short segments, so that individual segments can be broken off from this "bar" at the predetermined weak spots, which the short thin segments represent, and introduced into the machine. This "bar" principle can also be embodied in other geometric forms, for example vertical triangles which are only joined to one another at one of their longitudinal sides. In this case, it is appropriate for optical reasons to make the base of the triangle, by which the individual segments are interconnected, as one phase while the apex forms the second phase. In this embodiment, different coloring of the two phases is particularly attractive.

After pressing, the cleaning tablets have high stability. The fracture resistance of cylindrical tablets can be determined via the diametral fracture stress. This in turn can be determined in accordance with the following equation:

$$\sigma = \frac{2P}{\pi D t}$$

where σ represents the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure applied to the tablet that results in fracture thereof, D is the diameter of the tablet in meters and t is its height.

Examples

Two-phase laundry detergent tablets in the form of a two-layer tablet were produced by tabletting. Through the choice of the particular premixes, one of the two phases was blue in color while the other phase remained white. The blue coloration was obtained on the one hand by coloring a TAED-containing phase (C1, C2), the TAED additionally being colored blue in the case of Comparison Example 2. In Example E1 according to the invention, the bleach-containing phase was colored while the phase containing the bleach activator remained white. The composition of the detergent tablets, based on the particular phase, is shown in Table 1 below.

Table 1:

Detergent tablets - composition [% by weight]

	C1			C2			E1		
	Blue phase	White phase	Tab	Blue phase	White phase	Tab	Blue phase	White phase	Tab
Phase content [%]	23.3	76.6	100	23.3	76.6	100	28.0	72.0	100
Na percarbonate	-	42.0	32.20	-	42.0	32.20	42.0	27.0	31.20
TAED	50.0	-	11.67	-	-	-	-	13.5	9.73
TAED*	-	-	-	50.0	-	11.67	-	-	-
Na-SKS6	5.84	5.84	5.84	5.84	3.49	4.04	5.84	3.49	4.15
$NaHCO_3$	16.0	26.16	23.79	16.0	28.51	25.59	24.33	30.0	28.41
Citric acid	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
PEG 4000	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Disintegrator**	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PEG 400	0.25	-	0.06	0.25	-	0.06	0.25	-	0.07
Enzyme	1.88	-	0.44	1.88	-	0.44	1.55	-	0.43
Supranol® Blau	0.03	-	0.01	0.03	-	0.01	0.03	-	0.01

*: TAED colored with 0.03% by weight Supranol® Blau GLW (anthraquinone dye, trademark of Bayer AG)

**: Compacted cellulose (particle size: 90% by weight > 400 µm)

PEG: Polyethylene glycol with molecular weights of ~4000 or ~400 $gmole^{-1}$

Accordingly, contact between dye and bleach activator is at its most intensive in C1 and C2 while contact between dye and bleaching agent is at its most intensive in E1.

The tablets produced were individually packed in polypropylene bags (flow packs) and stored for 4 weeks at 30°C. After storage, the blue phases of Comparison Examples C1 and C2 show distinct and uneven fading and white patches while E1 shows a homogeneous blue phase with no significant lightening.

Color retention is distinctly better in the Example according to the invention than in the Comparison Examples.

CLAIMS

1. Two-phase or multi-phase cleaning tablets of compacted particulate detergent/cleaner comprising builder(s), bleaching agent, bleach activator(s) and optionally other ingredients of washing/cleaning compositions, wherein the bleach activator(s) is/are spatially separated from oxidation-sensitive substances in a demarcated region of the tablet.

2. Cleaning tablets as claimed in claim 1, wherein the demarcated region contains the bleach activator and other non-oxidation-sensitive ingredients of detergents/cleaners.

3. Cleaning tablets as claimed in claim 1 or 2, wherein the demarcated region contains the bleach activator and one or more substances from the group of builders, co-builders, surfactants, binders, disintegration aids and complexing agents.

4. Cleaning tablets as claimed in any of claims 1 to 3, wherein the demarcated region is free from bleaching agent(s).

5. Cleaning tablets as claimed in any of claims 1 to 4, wherein the bleaching agent and oxidation-sensitive substance(s) are present together in one region of the tablets.

6. Cleaning tablets as claimed in any of claims 1 to 5, wherein the tablets contain one or more substances from the group of dyes, optical brighteners, perfumes and enzymes as oxidation-sensitive substances.

7. Cleaning tablets as claimed in any of claims 1 to 6, wherein tetraacetyl ethylenediamine is used as the bleach activator.

8. Cleaning tablets as claimed in any of claims 1 to 7, wherein the demarcated region of the tablet is in the form of a separate layer, a coating or individual inserts.

9. Cleaning tablets as claimed in any of claims 1 to 8, wherein there is additionally present a disintegration aid, in quantities of 0.5 to 10% by weight, based on the weight of the tablet.

10. Cleaning tablets as claimed in any of claims 1 to 9, wherein the disintegration aid is a cellulose-based disintegration aid.

11. Cleaning tablets as claimed in any of claims 1 to 10, wherein the disintegration aid is in granular, co-granulated or compacted form.

12. Cleaning tablets as claimed in any of claims 1 to 11, wherein the disintegration aid is present in quantities of 3 to 7% by weight.

13. Cleaning tablets as claimed in any of claims 1 to 11, wherein the disintegration aid is present in quantities of 4 to 6% by weight.