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(54) **PROCEDE DE PRODUCTION DE TABLETTES DE DETERGENT
A DESAGREGATION RAPIDE**
(54) **A PROCESS FOR THE PRODUCTION OF RAPIDLY
DISINTEGRATING DETERGENT TABLETS**

(57) Detergent tablets distinguished both by high hardness values and hence transportation and handling stability and by excellent disintegration properties can be obtained by tableting in known manner if the premix to be tabletted has a temperature below 20°C immediately before tableting.

Abstract

Detergent tablets distinguished both by high hardness values and hence transportation and handling stability and by excellent disintegration properties can be obtained by tableting in known manner if the premix to be tableted has a temperature below 20°C immediately before tableting.

A Process for the Production of Rapidly Disintegrating Detergent Tablets

This invention relates to a process for the production of tablets having deterative properties. More particularly, the present invention relates to a process for the production of laundry detergent tablets for washing laundry in domestic washing machines which are referred to in short as
5 detergent tablets.

Nowadays, detergents are commercially available in the form of liquid or solid products. Solid products can be formulated as conventional powders or as concentrates obtainable, for example, by granulation or extrusion. Concentrated detergents have the advantage over conventional
10 powders that they are easier and less expensive to package and can be used in smaller doses per wash cycle. The reduced pack sizes also reduce transportation and storage costs. The most highly concentrated form in which detergents are commercially available in some countries are tablets. Whereas water softeners and dishwashing detergents are widely available
15 in tablet form, tableted laundry detergents pose various problems which, hitherto, have prevented their use on a wide scale and have been an obstacle to consumer acceptance. In view of the distinctly higher surfactant contents, the problems normally occurring with tablets are aggravated. Detergent tablets containing alkoxylated nonionic surfactants
20 are particularly problematical because surfactants belonging to this class have an adverse effect on the solubility of the tablets. On the other hand, the surfactants in question are particularly desirable by virtue of their high cleaning performance.

The dichotomy between a sufficiently hard tablet and a sufficiently
25 short disintegration time is a central problem. Since sufficiently stable, i.e. dimensionally stable and fracture-resistant, tablets can only be produced by relatively high tableting pressures, the tablet ingredients are heavily

compacted which leads to delayed disintegration of the tablet in the aqueous liquor and hence to slow release of the active substances during the washing or dishwashing process. Another disadvantage of the delayed disintegration of the tablets is that conventional detergent tablets cannot be introduced into the washing process from the dispensing compartment of dishwashing machines because the tablets do not disintegrate sufficiently quickly into secondary particles that are small enough to be flushed into the washing drum from the dispensing compartment.

Numerous attempts to solve this problem have been made in the prior art. In addition to the use of special ingredients intended to promote disintegration, the coating of individual ingredients or the entire tablet has also been proposed. These proposed solutions approach the problem so to speak "from the formulation angle", i.e. certain ingredients are used or the tablet or parts of the tablet is/are refined by additives. Besides these "chemical" solutions, attempts have also been made to solve the above-mentioned problem independently of the formulation. Most of these "physical" solutions are concerned with certain embodiments of tableting machines or other process parameters, the tableting pressure being of primary concern. It has also been proposed to sieve the premixes to be tableted to certain particle fractions which is supposed to provide the tablets with favorable properties irrespective of the composition of the premix.

Thus, **EP-A-0 466 484** (Unilever) discloses detergent tablets where the premix to be tableted has particle sizes of 200 to 1200 μm , the upper and lower limits to the particle size differing by no more than 700 μm . The surface treatment of individual ingredients is not mentioned in this document.

EP-A-0 522 766 (Unilever) relates to tablets of a compacted particulate detergent composition containing surfactants, builders and disintegration aids (for example based on cellulose), the particles being at least

partly coated with the disintegration aid which has both a binding and a disintegrating effect during dissolving of the tablets in water. This document also refers to the general difficulty of producing sufficiently stable, but at the same time readily dissolving tablets. The particle size in
5 the mixture to be tableted is said to be above 200 μm , the upper and lower limits to the individual particle sizes differing by no more than 700 μm .

DE 40 10 533 (Henkel KGaA) discloses a process for the production of tablets from precompacted granules. In this process, the granules produced in a first step by extrusion and size reduction are optionally mixed
10 with other ingredients and auxiliaries and the resulting mixtures are tableted. According to this document, the precompacted granules make up as much as 100% of the tablets. There is no mention of any pretreatment of the added components optionally used.

European patent application **EP 711 828** (Unilever) claims a process
15 for the production of detergent tablets by tableting a particulate composition containing a binder. The melting point of the binder is said to be between 35 and 90°C, the tableting process being carried out at temperatures below the melting point, but above 28°C. Accordingly, this document combines a "chemical" approach with a "physical" approach.

20 The advantage of the "physical" solutions described above is that they can be put into practice both irrespective of the composition of the premix and irrespective of the type of tableting machine used. As a result, the manufacturer is able to take more account of other basic conditions both in regard to the composition of his detergent tablets and in regard to
25 the acquisition and use of his machinery without having to be subjected to additional restrictions. Nevertheless, the detergent tablets produced in accordance with the cited documents still have disadvantages. Although they are sufficiently hard, they often have disintegration rates which do not allow them to be dosed from the dispensing compartment of a domestic
30 washing machine. In the cited prior-art documents, dissolving times of

under 10 minutes and residue levels of under 50% are described as good although values such as these are totally inadequate for the use of detergent tablets via a dispensing compartment.

Now, the problem addressed by the present invention was to provide
5 a process for the production of detergent tablets which would enable tablets without any of the disadvantages mentioned above to be produced. It would be possible in a simple and reproducible manner to produce detergent tablets which would combine high hardness with rapid disintegration and which could also be used via the dispensing compartment of a
10 washing machine. At the same time, the expert would be given the greatest possible freedom of choice in regard to composition and the choice of the press.

It has now been found that detergent tablets with the advantageous properties mentioned can be produced if the premixes to be tableted are
15 cooled and tableted at relatively low temperatures.

The present invention relates to a process for the production of detergent tablets by tableting in known manner in which the premix to be tableted has a temperature below 20°C immediately before tableting.

In a preferred embodiment of the invention, the premix to be
20 tableted has a temperature well below 20°C before tableting. Accordingly, variants of the process according to the invention are carried out in such a way that the premix to be tableted has a temperature below 18°C, preferably below 15°C, more preferably below 13°C and most preferably below 10°C immediately before tableting.

25 According to the invention, premixes with temperatures of 19°C or 17°C or 16°C or 14°C or 12°C or 11°C or 9°C or 8°C or 7°C or 6°C or 5°C or 4°C or 3°C or 2°C or 1°C or 0°C may of course also be tableted. According to the invention, premixes with temperatures below the freezing point may also be tableted, temperatures of -1°C, -2°C, -3°C, -4°C, -5°C,
30 -6°C, -7°C, -8°C, -9°C, -10°C, -11°C, -12°C, -13°C, -14°C, -15°C, -16°C,

-17°C, -18°C, -19°C or -20°C being mentioned by way of example, although the premix may have even lower temperatures.

In preferred embodiments of the process according to the invention, the premix to be tableted contains surfactant-containing granules and
5 other aftertreatment components. The surfactant-containing granules may be produced by conventional industrial granulation processes, such as compacting, extrusion, mixer granulation, pelleting or fluidized bed granulation. It is of advantage so far as the subsequent detergent tablets are concerned if the premix to be tableted has a bulk density approaching
10 that of typical compact detergents. In one particularly preferred embodiment, the premix to be tableted has a bulk density of at least 500 g/l, preferably of at least 600 g/l and more preferably of at least 700 g/l.

In preferred variants of the process, the surfactant-containing granules satisfy certain particle size criteria. Thus, preferred processes
15 according to the invention are characterized in that the surfactant-containing granules have particle sizes of 100 to 2000 µm, preferably 200 to 1800 µm, more preferably 400 to 1600 µm and most preferably 600 to 1400 µm.

Besides the active substances (anionic and/or nonionic and/or
20 cationic and/or amphoteric surfactants), the surfactant granules preferably contain carrier materials which, in one particularly preferred embodiment, emanate from the group of builders. Particularly advantageous processes are characterized in that the premix to be tableted contains surfactant-containing granules which contain anionic and/or nonionic surfactants and
25 builders and have total surfactant contents of 5 to 60% by weight, preferably 10 to 50% by weight and more preferably 15 to 40% by weight, based on the surfactant granules.

To develop their cleaning performance, the surfactant granules contain surfactants from the group of anionic, nonionic, zwitterionic or
30 cationic surfactants, anionic surfactants being distinctly preferred on

economic grounds and for their performance spectrum.

Suitable anionic surfactants are, for example, those of the sulfonate and sulfate type. Suitable surfactants of the sulfonate type are preferably C₉₋₁₃ alkyl benzenesulfonates, olefin sulfonates, i.e. mixtures of alkene and hydroxyalkane sulfonates, and the disulfonates obtained, for example, from C₁₂₋₁₈ 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 C₁₂₋₁₈ 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 oil, palm kernel oil 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 C₁₂₋₁₈ fatty alcohols, for example cocofatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or C₁₀₋₂₀ 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. C₁₂₋₁₆ alkyl sulfates, C₁₂₋₁₅ alkyl sulfates and C₁₄₋₁₅ 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 C₇₋₂₁ alcohols ethoxylated with 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C₉₋₁₁ alcohols containing on average 3.5 moles of ethylene oxide (EO) or C₁₂₋₁₈ 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 C₈₋₁₈ 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, palm kernel 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.

5 According to the invention, preferred detergent tablets are those which contain 5 to 50% by weight, preferably 7.5 to 40% by weight and more preferably 10 to 20% by weight of anionic surfactants, based on the weight of the tablet.

10 So far as the choice of anionic surfactants used in the detergent tablets according to the invention is concerned, there are no basic requirements to restrict the freedom of formulation. However, preferred surfactant tablets do have a soap content in excess of 0.2% by weight, based on the total weight of the detergent tablet. Preferred anionic surfactants are alkyl benzenesulfonates and fatty alcohol sulfates, preferred detergent tablets containing 2 to 20% by weight, preferably 2.5 to 15% by weight and more preferably 5 to 10% by weight of fatty alcohol sulfate(s), based on the weight of the detergent composition.

20 Preferred nonionic surfactants are alkoxyated, 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 component may be linear or, preferably, methyl-branched in the 2-position or may contain linear and methyl-branched residues in the form of the mixtures typically present in oxoalcohol residues. However, alcohol ethoxylates containing linear residues of alcohols of native origin with 12 to 18 carbon atoms, for example coconut, palm, tallow or oleyl alcohol, and on average 2 to 8 EO per mole of alcohol are particularly preferred. Preferred ethoxylated alcohols include, for example, C₁₂₋₁₄ alcohols containing 3 EO or 4 EO, C₉₋₁₁ alcohol containing 7 EO, C₁₃₋₁₅ alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, 25 C₁₂₋₁₈ alcohols containing 3 EO, 5 EO or 7 EO and mixtures thereof, such 30

as mixtures of C₁₂₋₁₄ alcohol containing 3 EO and C₁₂₋₁₈ 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.

Another class of preferred nonionic surfactants which may be used either as sole nonionic surfactant or in combination with other nonionic surfactants are alkoxyated, 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**.

Another class of nonionic surfactants which may advantageously be used are the alkyl polyglycosides (APGs). Suitable alkyl polyglycosides correspond to the general formula RO(G)_z where R is a linear or branched, more particularly 2-methyl-branched, saturated or unsaturated aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glucose unit containing 5 or 6 carbon atoms, preferably glucose. The degree of glycosidation z is between 1.0 and 4.0, preferably between 1.0 and 2.0 and more preferably between 1.1 and 1.4.

Linear alkyl polyglucosides, i.e. alkyl polyglycosides in which the polyglycosyl component is a glucose unit and the alkyl component is an n-alkyl group, are preferably used.

The detergent tablets according to the invention may advantageously contain alkyl polyglycosides, APG contents of more than 0.2% by weight, based on the tablet as a whole, being preferred. Particularly preferred detergent tablets contain APGs in quantities of 0.2 to

10% by weight, preferably in quantities of 0.2 to 5% by weight and more preferably in quantities of 0.5 to 3% by weight.

Nonionic surfactants of the amine oxide type, for example N-coconutalkyl-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):



in which RCO is an aliphatic acyl group containing 6 to 22 carbon atoms, R¹ 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):



in which R is a linear or branched alkyl or alkenyl group containing 7 to 12 carbon atoms, R¹ 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 polyhydroxy-alkyl group, of which the alkyl chain is substituted by at least two hydroxyl groups, or alkoxyated, preferably ethoxyated or propoxyated, derivatives
5 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
10 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**.

As mentioned above, the nonionic and anionic surfactants can be
15 incorporated in the detergent tablets according to the invention in various ways. They may be added to the premix to be tabletted, for example, in solid form or may be sprayed onto the premix in liquid form. It has been found to be of advantage to produce surfactant granules which are mixed with other powder-form components to form the premix to be tabletted and
20 tabletted. According to the invention, preferred detergent tablets contain the surfactants in the form of surfactant-containing granules which are present in the tablets in quantities of 40 to 95% by weight, preferably 45 to 85% by weight and more preferably 55 to 75% by weight, based on tablet weight.

25 In order to incorporate the required amount of detergent substance in the detergent tablets, preferred variants of the process are characterized in that the premix contains surfactant granules with surfactant contents of 5 to 60% by weight, preferably 10 to 50% by weight and more preferably 15 to 40% by weight, based on the weight of the surfactant granules (see
30 above). According to the invention, detergent tablets of which the

surfactant granules have anionic surfactant contents of 5 to 45% by weight, preferably 10 to 40% by weight and more preferably 15 to 35% by weight, based on the weight of the surfactant granules, and nonionic surfactant contents of 1 to 30% by weight, preferably 5 to 25% by weight and more preferably 7.5 to 20% by weight, based on the weight of the surfactant granules, are particularly preferred.

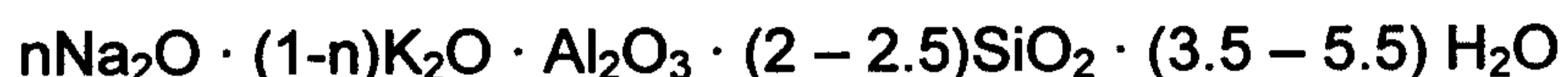
In order to obtain storage-stable free-flowing surfactant granules, carriers which contain the surfactant granules, i.e. builders, are preferably added in the production of the surfactant granules. Other detergent ingredients, more particularly so-called minor components, such as optical brighteners, polymers, defoamers, phosphonates, dyes and perfumes, may also form part of the surfactant granules. The substances are described in the following.

In the second step of the process according to the invention, the surfactant granules are mixed with other detergent ingredients to form a tabletable premix which is then tabletted. According to the invention, the production of detergent tablets is preferred so that preferred variants of the process according to the invention are characterized in that the surfactant-containing granules make up 40 to 95% by weight, preferably 45 to 85% by weight and more preferably 55 to 75% by weight - based on the weight of the detergent tablets - of the premix to be tabletted and hence of the detergent tablets.

As part of the surfactant granules, but also as an aftertreatment component optionally added to the premix, builders are important ingredients of detergents. Besides the detergents ingredients, builders are the most important ingredients of detergents. Any of the builders normally used in detergents may be present in the detergent tablets according to the invention, including in particular zeolites, silicates, carbonates, organic co-builders and also - providing there are no ecological objections to their use - phosphates.

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 also possible 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:

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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.

Crystalline layer-form sodium silicates suitable as builders correspond to the general formula $\text{NaMSi}_x\text{O}_{2x+1}\text{A} \cdot y \text{H}_2\text{O}$, 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 layer silicates such as these are described, for example, in European patent application **EP-A-0 164 514**. Preferred crystalline layer 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 $\text{Na}_2\text{Si}_2\text{O}_5\text{A} \cdot y \text{H}_2\text{O}$ 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 ($\text{Na}_2\text{O}:\text{SiO}_2$ 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

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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
5 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
10 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
15 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.

If desired, more zeolite besides the quantity of zeolite P and/or X
20 introduced through the surfactant granules may be incorporated in the premix by adding zeolite as an aftertreatment component. The finely crystalline, synthetic zeolite containing bound water used in accordance with the invention is preferably a zeolite of the A, P, X or Y type. However, zeolite X and mixtures of A, X and/or P are also suitable. Suitable zeolites
25 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.
30 The sodium salts of the orthophosphates, the pyrophosphates and, in

particular, the tripolyphosphates are particularly suitable.

Organic cobuilders which may be used in the detergent tablets according to the invention include, in particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, 5 polyacetals, dextrans, other organic cobuilders (see below) and phosphonates. Substances belonging to these classes are described in the following.

Useful organic builders are, for example, the polycarboxylic acids usable, for example, in the form of their sodium salts (polycarboxylic acids 10 in this context being understood to be carboxylic acids carrying more than one acid function). Examples include citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing its use is not ecologically unsafe, and mixtures thereof. Preferred salts are the salts 15 of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

The acids per se may also be used. Besides their builder effect, the acids typically have the property of an acidifying component and, accordingly, are also used to establish a lower and more mild pH value in 20 laundry or dishwashing detergents. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and mixtures thereof are particularly mentioned in this regard.

Other suitable builders are polymeric polycarboxylates such as, for example, the alkali metal salts of polyacrylic acid or polymethacrylic acid, 25 for example those having a relative molecular weight of 500 to 70,000 g/mole.

The molecular weights mentioned in this specification for polymeric polycarboxylates are weight-average molecular weights M_w of the particular acid form which, basically, were determined by gel permeation 30 chromatography (GPC) using a UV detector. The measurement was

carried out against an external polyacrylic acid standard which provides realistic molecular weight values by virtue of its structural similarity to the polymers investigated. These values differ distinctly from the molecular weights measured against polystyrene sulfonic acids as standard. The
5 molecular weights measured against polystyrene sulfonic acids are generally far higher than the molecular weights mentioned in this specification.

Suitable polymers are, in particular, polyacrylates which preferably have a molecular weight of 2,000 to 20,000 g/mole. By virtue of their
10 superior solubility, preferred representatives of this group are the short-chain polyacrylates which have molecular weights of 2,000 to 10,000 g/mole and, more particularly, 3,000 to 5,000 g/mole.

Also suitable are copolymeric polycarboxylates, particularly those of acrylic acid with methacrylic acid and those of acrylic acid or methacrylic
15 acid with maleic acid. Acrylic acid/maleic acid copolymers containing 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid have proved to be particularly suitable. Their relative molecular weight, based on the free acids, is generally in the range from 2,000 to 70,000 g/mole, preferably in the range from 20,000 to 50,000 g/mole and more preferably
20 in the range from 30,000 to 40,000 g/mole.

The (co)polymeric polycarboxylates may be used either in powder form or in the form of an aqueous solution. The content of (co)polymeric polycarboxylates in the compositions is preferably between 0.5 and 20% by weight and more preferably between 3 and 10% by weight.

25 In order to improve their solubility in water, the polymers may also contain allyl sulfonic acids, for example allyloxybenzenesulfonic acid and methallyl sulfonic acid as monomer.

Biodegradable polymers of more than two different monomer units are also particularly preferred, examples including those which contain
30 salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol

derivatives as monomers or those which contain salts of acrylic acid and 2-alkylallyl sulfonic acid and sugar derivatives as monomers.

Other preferred copolymers are those described in German patent applications **DE-A-43 03 320** and **DE-A-44 17 734** which preferably contain
5 acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

Other preferred builders are polymeric aminodicarboxylic acids, salts or precursors thereof. Polyaspartic acids or salts and derivatives thereof which, according to German patent application **DE-A-195 40 086**, have a
10 bleach-stabilizing effect in addition to their co-builder properties are particularly preferred.

Other suitable builders are polyacetals which may be obtained by reaction of dialdehydes with polyol carboxylic acids containing 5 to 7 carbon atoms and at least three hydroxyl groups. Preferred polyacetals are
15 obtained from dialdehydes, such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids, such as gluconic acid and/or glucoheptonic acid.

Other suitable organic builders are dextrans, for example oligomers or polymers of carbohydrates which may be obtained by partial hydrolysis
20 of starches. The hydrolysis may be carried out by standard methods, for example acid- or enzyme-catalyzed methods. The end products are preferably hydrolysis products with average molecular weights of 400 to 500,000 g/mole. A polysaccharide with a dextrose equivalent (DE) of 0.5 to 40 and, more particularly, 2 to 30 is preferred, the DE being an accepted
25 measure of the reducing effect of a polysaccharide by comparison with dextrose which has a DE of 100. Both maltodextrins with a DE of 3 to 20 and dry glucose syrups with a DE of 20 to 37 and also so-called yellow dextrans and white dextrans with relatively high molecular weights of 2,000 to 30,000 g/mole may be used.

The oxidized derivatives of such dextrans are their reaction products with oxidizing agents which are capable of oxidizing at least one alcohol function of the saccharide ring to the carboxylic acid function. Dextrans thus oxidized and processes for their production are known, for example, from
5 European patent applications **EP-A-0 232 202**, **EP-A-0 427 349**, **EP-A-0 472 042** and **EP-A-0 542 496** and from International patent applications **WO 92/18542**, **WO 93/08251**, **WO 93/16110**, **WO 94/28030**, **WO 95/07303**, **WO 95/12619** and **WO 95/20608**. An oxidized oligosaccharide according to German patent application **DE-A-196 00 018** is also suitable. A product
10 oxidized at C₆ of the saccharide ring can be particularly advantageous.

Other suitable co-builders are oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate. Ethylenediamine-N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. Glycerol disuccinates and glycerol trisuccinates are also
15 particularly preferred in this connection. The quantities used in zeolite-containing and/or silicate-containing formulations are from 3 to 15% by weight.

Other useful organic co-builders are, for example, acetylated hydroxycarboxylic acids and salts thereof which may optionally be present
20 in lactone form and which contain at least 4 carbon atoms, at least one hydroxy group and at most two acid groups. Co-builders such as these are described, for example, in International patent application **WO-A-95/20029**.

Another class of substances with co-builder properties are the phosphonates, more particularly hydroxyalkane and aminoalkane phosphonates. Among the hydroxyalkane phosphonates, 1-hydroxyethane-1,1-
25 diphosphate (HEDP) is particularly important as a co-builder. It is preferably used in the form of a sodium salt, the disodium salt showing a neutral reaction and the tetrasodium salt an alkaline reaction (pH 9). Preferred aminoalkane phosphonates are ethylenediamine tetramethylene
30 phosphonate (EDTMP), diethylenetriamine pentamethylene phosphonate

(DTPMP) and higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, for example as the hexasodium salt of EDTMP and as the hepta- and octasodium salt of DTPMP. Within the class of phosphonates, HEDP is preferably used as builder. The aminoalkane phosphonates also show a pronounced heavy metal binding capacity. Accordingly, it can be of advantage, particularly where the detergents also contain bleaching agents, to use aminoalkane phosphonates, more especially DTPMP, or mixtures of the phosphonates mentioned.

10 In addition, any compounds capable of forming complexes with alkaline earth metal ions may be used as co-builders.

The production of surfactant-containing granules is widely described in the prior art literature, including many patents and numerous synoptic articles and books. Thus, W. Hermann de Groot, I. Adami and G.F. Moretti describe various spray drying, mixing and granulation processes for the production of detergents in **"The Manufacture of Modern Detergent Powders"**, Hermann de Groot Academic Publisher, Wassenaar, 1995.

On energy grounds, the surfactant-containing granules are preferably produced by a granulation process and not by spray drying according to the invention. Besides conventional granulation and agglomeration processes, which may be carried out in various mixer-granulators and mixer-agglomerators, press agglomeration processes, for example, may also be used. Accordingly, processes in which the surfactant-containing granules are produced by granulation, agglomeration, press agglomeration or a combination of these processes are preferred.

The granulation process may be carried out in a number of machines typically used in the detergent industry. For example, the spheronizers widely used in the pharmaceutical industry may be employed. In rotary machines such as these, the residence time of the granules is normally less than 20 seconds. Conventional mixers and mixer-granulators

are also suitable for granulation. The mixers used may be both high-shear mixers and also normal mixers with lower rotational speeds. Suitable mixers are, for example, Series R or RV Eirich® mixers (trademarks of Maschinenfabrik Gustav Eirich, Hardheim), the Schugi® Flexomix mixer, 5 the Fukae® FS-G mixers (trademarks of Fukae Powtech, Kogyo Co., Japan), Lödige® FM, KM and CB mixers (trademarks of Lödige Maschinenbau GmbH, Paderborn) and Series T or K-T Drais® mixers (trademarks of Drais-Werke GmbH, Mannheim). The residence times of the granules in the mixers is less than 60 seconds, the residence time also 10 depending on the rotational speed of the mixer. The residence times are shorter, the higher the rotational speed of the mixer. The residence times of the granules in the mixer/spheronizer are preferably under one minute and more preferably under 15 seconds. In low-speed mixers, for example a Lödige KM, residence times of up to 20 minutes are adjusted, residence 15 times of under 10 minutes being preferred in the interests of process economy.

In the press agglomeration process, the surfactant containing granules are shear-compacted under pressure and, at the same time, homogenized and are then discharged from the machine via a 20 shaping/forming stage. Industrially the most important press agglomeration processes are extrusion, roll compacting, pelleting and tableting. Press agglomeration processes preferably used in accordance with the invention for producing the surfactant-containing granules are extrusion, roll compacting and pelleting.

25 In order to facilitate the disintegration of heavily 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 30 disintegration accelerators are auxiliaries which provide for 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 disintegrators are, for example, 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 detergent 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 the weight of the tablet.

According to the invention, preferred disintegrators are cellulose-based disintegrators, so that preferred detergent 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 tableted. 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 **WO 98/40463** (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 is mostly above 200 μm , 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 the 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
5 compacted, for example, to granules with a mean particle size of 200 μm .

According to the present invention, therefore, preferred processes are those in which the premix to be tableted additionally contains a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granulated, cogramulated or compacted form, in quantities of
10 0.5 to 10% by weight, preferably 3 to 7% by weight and more preferably 4 to 6% by weight, based on the weight of the premix.

In other preferred processes, the premix additionally contains one or more substances from the group of bleaching agents, bleach activators, enzymes, pH regulators, perfumes, perfume carriers, fluorescers, dyes,
15 foam inhibitors, silicone oils, redeposition inhibitors, optical brighteners, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors. The substances are described in the following.

Among the compounds yielding H_2O_2 in water which serve as bleaching agents, sodium perborate tetrahydrate and sodium perborate
20 monohydrate are particularly important. Other useful bleaching agents are, for example, sodium percarbonate, peroxyphosphates, citrate perhydrates and H_2O_2 -yielding peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecane dioic acid. Even where the bleaching agents are used, there is
25 no need for surfactants and/or builders so that pure bleach tablets can be produced. If pure bleach tablets are to be used in the washing of laundry, a combination of sodium percarbonate and sodium sesquicarbonate is preferred irrespective of the other ingredients present in the tablets. If detergent or bleach tablets for dishwashing machines are being produced,
30 bleaching agents from the group of organic bleaches may also be used.

Typical organic bleaching agents are diacyl peroxides, such as dibenzoyl peroxide for example. Other typical organic bleaching agents are the peroxy acids, of which alkyl peroxy acids and aryl peroxy acids are particularly mentioned as examples. Preferred representatives are (a) peroxybenzoic acid and ring-substituted derivatives thereof, such as alkyl peroxybenzoic acids, but also peroxy- α -naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxyauric acid, peroxysearic acid, ϵ -phthalimidoperoxypropionic acid [phthaliminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxypropionic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxydicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyl-di(6-aminopercaproic acid).

Other suitable bleaching agents in dishwasher tablets are chlorine- and bromine-releasing substances. Suitable chlorine- or bromine-releasing materials are, for example, heterocyclic N-bromamides and N-chloramides, for example trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations, such as potassium and sodium. Hydantoin compounds, such as 1,3-dichloro-5,5-dimethyl hydantoin, are also suitable.

In order to obtain an improved bleaching effect where washing is carried out at temperatures of 60°C or lower, bleach activators may be incorporated in the detergent tablets according to the invention. The bleach activators may be compounds which form aliphatic peroxocarboxylic acids containing preferably 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Substances bearing O- and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups are suitable. Preferred bleach activators are polyacylated

alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more particularly tetraacetyl glycoluril (TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more particularly phthalic anhydride, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

10 In addition to or instead of the conventional bleach activators mentioned above, 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, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl
15 complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and cobalt-, iron-, copper- and ruthenium-ammine complexes may also be used as bleach catalysts.

Suitable enzymes are those from the class of proteases, lipases,
20 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
25 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
30 shell-forming substances 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.

5 In addition, the detergent tablets according to the invention may also contain components with a positive effect on the removability 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-
10 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
15 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.

20 The tablets may contain derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. 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,
25 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
30 used.

Dyes and perfumes are added to the detergent 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 perfumes 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 carbonyl 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 fragrance 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 detergent tablets according to the invention normally contain less than 0.01% by weight of dyes whereas perfumes can make up as much as 2% by weight of the formulation as a whole.

The perfumes may be directly incorporated in the detergents 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.

In order to improve their aesthetic impression, the detergents 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.

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, tableting) and the final detergent 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 compound 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.

According to the invention, preferred processes for the production of detergent tablets are those in which the, or one of the, aftertreatment components subsequently incorporated is a zeolite of the faujasite type

with particle sizes below 100 μm , preferably below 10 μm and more preferably below 5 μm and makes 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 tableted.

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

The premix is first introduced into the die, the filling level and hence the weight and shape of the tablet formed being determined by the position
15 of the lower punch and the shape of the die. Uniform dosing, even at high tablet throughputs, is preferably achieved by volumetric dosing of the compound. As the tableting process continues, the top punch comes into contact with the premix and continues descending towards the bottom punch. During this compaction phase, the particles of the premix are
20 pressed closer together, the void volume in the filling between the punches continuously diminishing. The plastic deformation phase in which the particles coalesce and form the tablet begins from a certain position of the top punch (and hence from a certain pressure on the premix). Depending on the physical properties of the premix, its constituent particles are also
25 partly crushed, the premix sintering at even higher pressures. As the tableting rate increases, i.e. at high throughputs, the elastic deformation phase becomes increasingly shorter so that the tablets formed can have more or less large voids. In the final step of the tableting process, the tablet is forced from the die by the bottom punch and carried away by
30 following conveyors. At this stage, only the weight of the tablet is

definitively established because the tablets can still change shape and size as a result of physical processes (re-elongation, crystallographic effects, cooling, etc.).

The tableting 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 tableting 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. Tableting 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 tableting 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 compound can be individually adjusted through the tools for the top and bottom punches, pressure being built up by the rolling of the punch
5 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 multiple-layer tablets, several filling shoes are arranged one behind the other without the lightly compacted first layer
10 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
15 multiple punches so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be simultaneously used for tableting. Modern rotary tablet presses have throughputs of more than one million tablets per hour.

Where rotary presses are used for tableting, it has proved to be of
20 advantage to carry out the tableting process with minimal variations in the weight of the tablets. Variations in tablet hardness can also be reduced in this way. Minimal variations in weight can be achieved as follows:

- using plastic inserts with minimal thickness tolerances
- low rotor speed
- 25 – large filling shoe
- adapting the rotational speed of the filling shoe blade to the rotor speed
- filling shoe with constant powder height
- decoupling the filling shoe from the powder supply

Any of the nonstick coatings known in the art may be used to reduce
30 caking on the punch. Plastic coatings, plastic inserts or plastic punches are

particularly advantageous. Rotating punches have also proved to be of advantage; if possible, the upper and lower punches should be designed for rotation. If rotating punches are used, there will generally be no need for a plastic insert. In that case, the surfaces of the punch should be
5 electropolished.

It has also been found that long tableting times are advantageous. These can be achieved by using pressure rails, several pressure rollers or low rotor speeds. Since variations in tablet hardness are caused by variations in the pressures applied, systems which limit the tableting
10 pressure should be used. Elastic punches, pneumatic compensators or spring elements in the force path may be used. The pressure roller can also be spring-mounted.

Tableting machines suitable for the purposes of the invention can be obtained, for example, from the following companies: Apparatebau
15 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 tableting machine is the model HPF 630 hydraulic double-pressure press
20 manufactured by LAEIS, D.

The tablets can be made in certain shapes and certain sizes. 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
25 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. However, it is also possible to form pressings which combine several such
30 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 according to the invention 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. However, it is of course readily possible - and preferred in accordance with the present invention - to use the detergent tablets in conjunction with a dosing aid.

Another preferred 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 another possible embodiment, however, the various components are not compressed to form a single tablet, instead the tablets obtained comprise several layers, i.e. at least two layers. These various layers may have different dissolving rates. This can provide the tablets with favorable performance properties. If, for example, the tablets contain components which adversely affect one another, one component may be integrated in the more quickly dissolving layer while the other component may be incorporated in a more slowly dissolving layer so that the first component

can already have reacted off by the time the second component dissolves. The various layers of the tablets can be arranged in the form of a stack, in which case the inner layer(s) dissolve at the edges of the tablet before the outer layers have completely dissolved. Alternatively, however, the inner
5 layer(s) may also be completely surrounded by the layers lying further to the outside which prevents constituents of the inner layer(s) from dissolving prematurely.

In another preferred embodiment of the invention, a tablet consists of at least three layers, i.e. two outer layers and at least one inner layer, a
10 peroxy bleaching agent being present in at least one of the inner layers whereas, in the case of the stack-like tablet, the two cover layers and, in the case of the envelope-like tablet, the outermost layers are free from peroxy bleaching agent. In another possible embodiment, peroxy
15 bleaching agent and any bleach activators or bleach catalysts present and/or enzymes may be spatially separated from one another in one and the same tablet. Multilayer tablets such as these have the advantage that they can be used not only via a dispensing compartment or via a dosing unit which is added to the wash liquor, instead it is also possible in cases
20 such as these to introduce the tablet into the machine in direct contact with the fabrics without any danger of spotting by bleaching agent or the like.

Similar effects can also be obtained by coating individual constituents of the detergent composition to be compressed or the tablet as a whole. To this end, the tablets to be coated may be sprayed, for example, with aqueous solutions or emulsions or a coating may be
25 obtained by the process known as melt coating.

After pressing, the detergent 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:

35

$$\Phi = \frac{2P}{BDt}$$

5 where Φ 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.

The present invention also relates to the use of cooled premixes with temperatures below 20°C for the production of detergent tablets. This use
10 of the cooled premixes in accordance with the invention leads to tablets with advantageous properties, as the following Examples show. The foregoing observations on the process according to the invention apply equally to preferred embodiments of the use according to the invention (lower temperatures, composition of the premix, etc.).

15

Examples

Surfactant granules of which the composition is shown in Table 1 were produced by wet granulation in a 130-liter Lödige plowshare mixer. After granulation, the granules were dried in an Aeromatic fluidized bed
20 dryer for 30 minutes at an inflowing air temperature of 60°C. After drying, the granules were sieved to remove the fine particles (< 0.4 mm) and coarse fractions (> 1.6 mm).

The surfactant granules were then mixed with other components to form a compressible premix of which the composition is shown in Table 2. The compressible premix was divided in half and each half was packed in an air-tight pack. The two halves of the premix were stored for 18 h at different temperatures (9°C according to the invention, room temperature - 22°C - in the Comparison Example), unpacked and tabletted in a Korsch eccentric press (tablet diameter 44 mm, height 22 mm, weight 37.5 g). The measured tablet hardnesses and disintegration times are the mean values of a double determination, the individual values varying by at most 2 N and

2 s, respectively, according to the type of tablet. Table 2, which shows the composition of the premixes, also indicates the temperature of the particular premix immediately before tableting.

Table 1: Composition of the surfactant granules [% by weight]

C₉₋₁₃ Alkyl benzenesulfonate	19.4
C₁₂₋₁₈ Fatty alcohol sulfate	5.2
C₁₂₋₁₈ Fatty alcohol + 7EO	4.8
Soap	1.6
C₁₂₋₁₆ Fatty alcohol-1,4-glucoside	1.0
Sodium carbonate	17.0
Zeolite A	28.5
Sodium silicate	5.6
Na Hydroxyethane-1,1-diphosphonate	0.8
Acrylic acid/maleic acid copolymer	5.6
Optical brightener	0.3
Water, salts	Balance

Table 2: Composition of the premixes [% by weight]

	E	C
Surfactant granules (Table 1)	62.9	62.9
Sodium percarbonate	17.0	17.0
TAED	7.3	7.3
Foam inhibitor	3.5	3.5
Enzymes	1.7	1.7
Repel-O-Tex® SRP 4*	1.1	1.1
Perfume	0.5	0.5
Wessalith® P (zeolite A)	1.0	1.0
Disintegration aid (cellulose)	5	5
Temperature of the premix before tableting [°C]	9.8	21.4

* Terephthalic acid/ethylene glycol/polyethylene glycol ester (Rhodia, Rhône-Poulenc)

The hardness of the tablets was measured after two days' storage by deforming a tablet until it broke, the force being applied to the sides of the tablet and the maximum force withstood by the tablet being determined.

To determine tablet disintegration, a tablet was placed in a glass beaker filled with water (600 ml water, temperature 30°C) and the time taken by the tablet to disintegrate completely was measured. The experimental data are set out in Table 3:

Table 3: Detergent tablets [physical data]

Tablet	E	C
Tablet hardness [N]	40	39
Disintegration time [s]	9	11
Tablet hardness [N]	49	52
Disintegration time [s]	13	24
Tablet hardness [N]	58	61
Disintegration time [s]	28	48

Table 3 shows that the disintegration times of detergent tablets are distinctly reduced by the process according to the invention which provides for distinct improvements, particularly in the case of relatively hard tablets.

CLAIMS

1. A process for the production of detergent tablets by tableting in known manner, characterized in that the premix to be tableted has a temperature below 20°C immediately before tableting.
- 5 2. A process as claimed in claim 1, characterized in that the premix to be tableted has a temperature below 18°C, preferably below 15°C, more preferably below 13°C and most preferably below 10°C before tableting.
3. A process as claimed in claim 1 or 2, characterized in that the
10 premix to be tableted contains surfactant-containing granules and other
aftertreatment components.
4. A process as claimed in claim 3, characterized in that the premix to be tableted contains surfactant-containing granules which contain anionic and/or nonionic surfactants and builders and of which the total surfactant content is 5 to 60% by weight, preferably 10 to 50% by weight and more
15 preferably 15 to 40% by weight, based on the surfactant granules.
5. A process as claimed in claim 3 or 4, characterized in that the surfactant-containing granules have particle sizes of 100 to 2,000 µm, preferably 200 to 1,800 µm, more preferably 400 to 1,600 µm and most preferably 600 to 1400 µm.
- 20 6. A process as claimed in any of claims 3 to 5, characterized in that the surfactant-containing granules make up 40 to 95% by weight, preferably 45 to 85% by weight and more preferably 55 to 75% by weight of the detergent tablets based on their weight.
7. A process as claimed in any of claims 1 to 6, characterized in that
25 the premix to be tableted has a bulk density of at least 500 g/l, preferably of at least 600 g/l and more preferably of at least 700 g/l.
8. A process as claimed in any of claims 1 to 7, characterized in that the premix to be tableted additionally contains a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, co-
30 granulated or compacted form, in quantities of 0.5 to 10% by weight,

preferably 3 to 7% by weight and more preferably 4 to 6% by weight, based on the weight of the premix.

9. A process as claimed in any of claims 3 to 8, characterized in that the, or one of the, aftertreatment components subsequently incorporated is
5 a zeolite of the faujasite type with particle sizes below 100 μm , preferably below 10 μm and more preferably below 5 μm and makes 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 tabletted.

10. A process as claimed in any of claims 1 to 9, characterized in that
10 the premix to be tabletted additionally contains one or more substances from the group of bleaching agents, bleach activators, enzymes, pH regulators, perfumes, perfume carriers, fluorescers, dyes, foam inhibitors, silicone oils, redeposition inhibitors, optical brighteners, discoloration inhibitors, dye transfer inhibitors and corrosion inhibitors.

15 11. The use of cooled premixes with temperatures below 20°C for the production of detergent tablets.